U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-261 128

Meyers Process Development for Chemical Desulfurization of Coal. Volume I

TRW Systems Group, Redondo Beach, Calif

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

May 76

348012

PB 261 128

EPA-600/2-76-143a
May 1976

Environmental Protection Technology Series

UNITED STATES · ENVIRONMENTAL PROTECTION AGENCY ·

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-143a	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Meyers Process Development for Chemical Desulfurization of Coal, Volume I		5. REPORT DATE May 1976
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) E. P. Koutsoukos, M. L. Kraft, R. A. Orsini, R. A. Meyers, M. J. Santy, and L. J. Van Nice		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS TRW Systems Group One Space Park Redondo Beach, California 90278		10. PROGRAM ELEMENT NO. 1AB013; ROAP 21AFJ-033
		11. CONTRACT/GRANT NO. 68-02-1336
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 6/73-12/75
		14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES Project officer L. Lorenzi, Jr. is no longer with EPA; for details contact Lewis D. Tamny, Mail Drop 61, Ext 2851.

16. ABSTRACT The report gives results of bench-scale development of the Meyers Process (for chemical removal of sulfur from coal) for desulfurization of both fine and coarse coal. More than 90% of the pyrite was removed from run-of-mine (ROM) fine coal and clean coarse coal, and more than 80% of the pyrite from ROM coarse coal. Process improvements were demonstrated involving: increased process slurry solids concentration for higher process throughput (33% w/w); lowered filtration requirements through use of larger top-size fine coal; and generated elemental sulfur removal by vaporization from the coal matrix. Pyrite leaching and reagent regeneration rate expressions were validated. Engineering studies showed that: the process may be engineered in a number of basic designs including simultaneous leach and regeneration, separate leach and regeneration, use of oxygen or air for regeneration, fine or coarse coal processing, and combined with coal cleaning; these process designs lead to stand-alone full capital cost estimates of \$30-80/KW of power plant nameplate capacity for the various process plant cases. Assuming ROM coal costs of \$0.81/MM Btu, the required market price of the desulfurized coal ranges from \$1.14 to \$1.32/MM Btu on a utility financed basis and \$1.41 to \$1.86/MM Btu on an investor financed basis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Coal	Stationary Sources	08G, 21D
Desulfurization	Meyers Process	07A, 07D
Pyrite	Chemical Coal Cleaning	

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 309
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE \$9.75/3.00

EPA Form 2220-1 (9-73)

1a

EPA-600/2-76-143a
May 1976

MEYERS PROCESS DEVELOPMENT FOR CHEMICAL DESULFURIZATION OF COAL

VOLUME I

by

E.P. Koutsoukos, M.L. Kraft, R.A. Orsini,
R.A. Meyers, M.J. Santy, and L.J. Van Nice

TRW Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. 68-02-1336
ROAP No. 21AFJ-033
Program Element No. 1AB013

EPA Project Officer: L. Lorenzi, Jr.

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ABSTRACT

The Meyers Process for chemical removal of sulfur from coal was tested at bench-scale for desulfurization of both fine and coarse coal. In excess of 90 percent of the pyrite was removed from run-of-mine fine coal and clean coarse coal and over 80 percent of the pyrite from run-of-mine coarse coal. Process unit improvements involving 1) increased process slurry solids concentration for higher process throughput (33% w/w), 2) lowered filtration requirements through use of larger top-size fine coal and 3) generated elemental sulfur removal by vaporization from the coal matrix were demonstrated. Pyrite leaching and reagent regeneration rate expressions were validated. Engineering studies showed that 1) the process may be engineered in a number of basic design configurations including simultaneous leach and regeneration, separate leach and regeneration, use of oxygen or air for regeneration, fine coal or coarse coal processing, and combination with coal cleaning; 2) these process design schemes lead to stand-alone full capital cost estimates of \$30-80/KW of power plant name plate capacity; 3) estimated coal desulfurization costs, annualized on a utility financed basis, range between \$0.33 and \$0.51/MM Btu, and 4) assuming ROM coal costs of \$20/ton, the costs of the desulfurized fuel are estimated to range between \$1.14 and \$1.32/MM Btu.

TABLE OF CONTENTS

Page

Abstract iii

List of Figures ix

List of Tables xiv

Acknowledgments xvi

Metric Conversion Factors xvii

Conclusions 1

Recommendations 6

1. Introduction 7

2. Pyritic Sulfur Removal from Suspendable Coal 11

  2.1 Coal Selection and Sample Preparation 11

  2.2 Coal Processing Experimentation 17

  2.3 Coal Processing Data 24

  2.4 Data Discussion and Interpretation 35

    2.4.1 Mixer Unit Operation 40

    2.4.2 L-R Unit Operation 50

      2.4.2.1 Pyrite Leaching Rates During L-R Processing of L.K. Coal at 120°C 56

      2.4.2.2 Reagent Regeneration During L-R Processing 68

      2.4.2.3 Temperature Effects on L-R Processing of of L.K. Coals 76

      2.4.2.4 Coal Top Size Effects During L-R Processing 82

      2.4.2.5 Slurry Concentration Effects 85

      2.4.2.6 Reagent Composition Effects 86

      2.4.2.7 Oxygen Partial Pressure Effects 95

    2.4.3 Settler Unit Operation 95

Preceding page blank

TABLE OF CONTENTS (continued)

Page

2.4.4 Coal Washing Operation 99

2.4.5 Elemental Sulfur Recovery Operation 101

2.4.5.1 Elemental Sulfur Recovery with Toluene 101

2.4.5.2 Elemental Sulfur Recovery with Hexane 107

2.4.5.3 Elemental Sulfur Vaporization 108

2.5 Solid-Liquid Separation Unit Operations 112

2.6 Coal Drying Operation 114

2.7 Principal Conclusions from Bench-Scale Data 114

2.8 L-R Processing of Upper Freeport Seam Coal 122

3. Reagent Recyclability-Trace Element Data 127

4. Processing of Coarse Coal 135

4.1 L-R Processing Data for Coarse Coal 136

4.2 Clean Coal Gravity Fraction Processing 139

4.3 Preliminary Data on Coarse Coal Processing by Size Fraction 141

5. Process Engineering 145

5.1 Suspendable Coal Processing 145

5.1.1 Design Basis for Suspendable Coal 146

5.1.2 Process Baseline Design 153

5.1.2.1 Conceptual Design for Commercial Scale 157

5.1.2.2 Process Cost Estimate 172

5.1.3 Process Trade-off Studies 180

5.1.3.1 Reactor Model 181

5.1.3.2 Pressure Effect 183

5.1.3.3 Iron Concentration Effect 188

TABLE OF CONTENTS (continued)

Page

5.1.3.4 Oxygen Purity 190

5.1.3.5 Compressed Air Regeneration 192

5.1.3.6 Three Reactor Configuration 196

5.1.3.7 Additional Studies 197

5.2 Coarse Coal (-1/4 inch) Processing 198

5.2.1 Concept Development 198

5.2.2 Conceptual Process Details 202

5.2.2.1 Reactor Section - Pit and Continuous 202

5.2.2.2 Regenerator Section - Pit and Continuous 206

5.2.2.3 Sulfate Removal Section 207

5.2.2.4 Coal Washing and Filtration Sections 209

5.2.2.5 Sulfur Removal Section 210

5.2.2.6 Energy Balance 210

5.2.3 Process Cost Estimate 210

5.3 Projection of Process Economics 215

5.3.1 Processing Option Description 215

5.3.2 Economics Model Description 219

5.3.3 Process Economics Evaluations 225

6. Chemical Analysis Studies 231

6.1 Adequacy of Standard Sulfur Analysis Techniques for Determining Meyers Process Performance 232

6.2 Meyers Process Monitoring Techniques 242

7. Materials Compatibility 249

7.1 Literature Survey and Alloy Selection Criteria 250

7.2 Experimental Corrosion Static Test Program 253

TABLE OF CONTENTS (continued)

Page

7.2.1 Experimental Method 253

7.2.2 Initial Runs and Modifications 257

7.2.3 Results and Conclusions of the Bomb Test 261

7.2.4 Conclusions and Recommendations 281

7.3 Dynamic Testing 282

8. References 291

9. Glossary of Abbreviations and Symbols 293

LIST OF FIGURES

No.		Page
1	Basic Bench-Scale Processing Scheme for the Removal of Pyritic Sulfur from Coal	18
2	Bench-Scale Coal Leaching and Reagent Regeneration Apparatus	19
3	Pyritic Sulfur Removal from 14 Mesh Top Size L.K. Coal Processed at 120°C with 5 Wt. % Fe Reagent	38
4	Typical Mixer Processing Conditions	44
5	100 Mesh Top Size Lower Kittanning Coal Leached with 5 Wt. % Fe Reagent	59
6	Pyrite Leaching Rate Constant Data	66
7	Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 120°C	70
8	Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 110°C	71
9	Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 130°C	72
10	Temperature Effect on L-R Processing of 100 Mesh Top Size L.K. Coal (20 Wt. Percent Slurries)	77
11	Temperature Effect on L-R Processing of 14 Mesh Top Size L.K. Coal (33 Wt. Percent Slurries)	78
12	Arrhenius Plots of Pyrite Leaching Rate Constants	83
13	Coal Top Size Effect on L-R Processing of Suspendable L.K. Coal	84
14	Slurry Concentration Effect on L-R Processing of Suspendable L.K. Coal	87
15	Effect of Total Iron Concentration on Pyrite Removal During L-R Processing of Suspendable L.K. Coals	94
16	Effect of Oxygen Partial Pressure on L-R Processing of Suspendable L.K. Coal	96
17	Vapor Pressure of Sulfur	110
18	Typical Process Design Curves	120

LIST OF FIGURES (continued)

No. Page

19 Upper Freeport Coal Leaching with 5 Wt. % Fe Reagent 123
20 Pyrite Leaching Rates from Upper Freeport and L.K. Mine Coals 124
21 Pyritic Sulfur Removal from ROM and Cleaned L.K. Coal at 102°C 140
22 Filtration Rate Correlation 154
23 Block Diagram for Fine Coal 155
24 Process Flow Diagram for Fine Coal 158
25 Simplified Reactor System 184
26 Reactor Residence Times as a Function of Oxygen Pressure in R-1 185
27 Effect of Pressure and Residence Time on Ferrous Iron Make 187
28 Reactor System Coat as a Function of Oxygen Pressure 189
29 Oxygen Circulation Diagram 191
30 Coarse Coal Process Schematic 201
31 Pit Reactor Schematic 203
32 Continuous Reactor Schematic 205
33 Sulfate Removal Section Schematic 208
34 Process Economics Case Block Diagram 217
35 Bomb Test Assembly 255
36 Composite Welded Tube Used in Test 255
37 Test Coupon Stack 256
38 Comparison of Corroded and Control Tubes 260
39 Microstructure of 304 Test Coupon After 1000 Hours Exposure 263
40 Microstructure of 304 Test Coupon at 400x Showing Sensitization at Grain Boundaries 263
41 Microsturcture of Unexposed Sample of 304 Test Coupon 264

LIST OF FIGURES (continued)

No.		Page
42	Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure	266
43	Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure	266
44	Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure	267
45	Edge of 316 Control Sample Showing Elongated Stringers Due to the Tensile Test	268
46	Edge of Exposed Test Coupon of 316 Showing Transgranular Cracks Extending Inward from Cut Edge	268
47	Edge of 316L Control	269
48	Edge of Exposed 316L Showing Crack Extension Along Crack Sensitive Corroded Paths and Pitting	269
49	Edge of 347 Control	270
50	Edge of Exposed Coupon of 347 Showing Limited Extension of Cracks in the Interior	270
51	Edge of Incoloy 825 Control	271
52	Edge of Exposed Incoloy 825 Test Coupon	271
53	Weld Between 304 and 304L in the Control Tube Sample	272
54	Weld Between 304 and 304L Tubes Showing Severe Corrosion Effects After Exposure	272
55	Outer Diameter of 304 Tube After Exposure Showing Corrosion Along the Edge and Pits on Surface	273
56	Inner Edge of Exposed 304L Tubing Showing Corroded Areas	274
57	Exposed Tube Sample	275
58	Exposed 316L Tube	276
59	I.D. of Exposed Armco Tubing Showing Some Cracks and Corroded Areas	277

LIST OF FIGURES (continued)

No. Page

60 O.D. of Exposed Armco Tubing Showing Stringers Along the Tube Drawing Axis and Light Pitting 277

61 O.D. of Exposed 316L Tubing Showing Corrosion Pits 278

62 I.D. of Exposed 316L Tubing Showing Less Severe Corrosion 278

63 Composite Tube Used in Dynamic Test 284

64 Composite Welded Tubing: Corrosion Effects in the Tube Interior 285

65 Section of Armco Tubing Interior 286

66 Section of 304 Tubing Interior 286

67 Weld Zone of Armco-304 Showing Chilled Structure and Sensitization by Chromium Carbide 287

68 Structure of 304 Away from Weld 287

69 Weld Zone of 316L-321 Showing Sensitization 288

70 Weld Zone of 304L-Carpenter 20 Cb/3 Showing Chilled Structure and Grain Boundary Sensitization 288

LIST OF TABLES

No.		Page
1	Raw Lower Kittanning Coal Analyses	13
2	Lower Kittanning Coal Ash Composition	15
3	Lower Kittanning Coal Particle Size Distribution	16
4	Rate Data on L-R Processing of 100 Mesh Top Size L.K. Coal with 3 Wt. % Iron Solution at 120°C and 100 Psig	27
5	Rate Data on L-R Processing of 100 Mesh Top Size L.K. Coal with 5 Wt. % Iron Solution at 120°C and 100 Psig	31
6	Process Mass Balance Data	33
7	Pyrite Removal from Coal with Iron Sulfate Solution at 102°C and Ambient Pressure	47
8	Measured and Predicted Pyrite Removal at the "Mixer Unit Operation"	51
9	Analyzed and Predicted Pyritic Sulfur Content of 100 Mesh Top Size L.K. Coal as a Function of L-R Processing Time at 120°C	61
10	Analyzed and Predicted Pyritic Sulfur Content of 14 Mesh Top Size L.K. Coal as a Function of L-R Processing Time at 120°C	62
11	Analyzed and Predicted S_p of L.K. Coal as a Function of L-R Processing Time at 110°C and 130°C	81
12	Pyrite Removal in the Settler Operation	98
13	Typical Wash Section Data from L-R Processed L.K. Coals	101
14	Elemental Sulfur Product Recovery from the L-R Processing of L.K. Coal	105
15	Elemental Sulfur Recovery by Successive Stages of Hexane-Toluene Leaching	109
16	Vaporization of Elemental Sulfur from Ferric Sulfate Leached Coal	111
17	Trace Element Analysis Accuracy Verification	129

LIST OF TABLES (continued)

No.		Page
18	Coal and Reagent Trace and Minor Elements	131
19	Trace Cation Content of Calcium Precipitates Recovered from Spent Reagent	133
20	L-R Processing of 3/8 Inch x 0 L.K. Coal in 5 Wt. % Fe Reagent at 120°C and 100 Psig	137
21	Pyritic Sulfur Removal from 1/4 Inch x 0 L.K. Coal at 102°C	138
22	Chemical Removal of Pyritic Sulfur from Cleaned 8 x 14 Mesh Lower Kittanning Coal at 102°C	139
23	Pyrite Leaching of 1/4 Inch x 0 Lower Kittanning Coal at 102°C	141
24	Preliminary Data on the Chemical Removal of Pyritic Sulfur from Size-Fractions of Lower Kittanning Coal at 102°C	142
25	Process Mass Balance for Fine Coal	162
26	Coal Desulfurization Process Equipment List	173
27	Sources of Equipment Cost Information	178
28	Sources of Operating Cost Information	180
29	Effect of Inert Gas Buildup on Reactor Section Annual Cost	193
30	Effect of Compressed Air on Reactor Section Annual Cost	195
31	Equipment Costs for a Three-Reactor Configuration	197
32	Coarse Coal Process Equipment Lists	213
33	Annualized Costs for Battery Limits Desulfurization Plants	214
34	Economic Evaluation Criteria	224
35	Constants for Use in Economics Evaluations	225
36	Case 1, Cleaned Fine Coal	226
37	Case 2, ROM Coarse Coal	227
38	Case 3, Deep Cleaned Fine Coal with 50% Meyers Process Bypass	278

LIST OF TABLES (continued)

No.		Page
39	Case 4, Deep Cleaned Coarse Coal with 50% Meyers Process Bypass	229
40	Upgrading Processing Costs	230
41	Comparison of Total Sulfur Analysis Techniques	236
42	Coal Sulfur Forms Analysis Investigations - Comparison of Techniques and Effect of Coal Digestion Time	240
43	Comparison of Corrosion Rates of Armco and 316/316L Steels	252
44	Corrosion Data from Literature on 304 and 316SS	253
45	Corrosion Data from Literature on Various Alloys	254
46	List of Materials Tested	258
47	Ferric Sulfate Corrosive Medium	259
48	Compilation - Coal Corrosion Material Evaluation	262
49	Changes in Mechanical Properties of Alloys After Exposure to Iron Sulfate Solution	280
50	Summary of Qualitatively Observed Events During Corrosion Testing	281

ACKNOWLEDGMENTS

The authors wish to acknowledge the valuable assistance received in this project from the following TRW personnel: L. Ledgerwood, S. Ziegler, and D. Kilday for substantial assistance in the experimentation; C. Murray and M. Wong for assistance rendered in process economics; D. Hopp for assistance in computer programming; J. Blumenthal and B. Dubrow for managerial assistance and manuscript review; and L. Broberg, M. Ramirez, and V. Melough for technical typing; special acknowledgment is due to V. Butler who undertook the difficult and arduous task of report coordination and finalization.

The authors owe appreciation to Lloyd Lorenzi, Jr., the monitoring Project Officer for the Environmental Protection Agency under this contract for his constant interest, cooperation and valuable comments on the project, and to T. Kelly Janes, also of EPA, for guidance and encouragement.

Gratitude is due to A. W. Deurbrouck of the U.S. Bureau of Mines (Bruceton, Pennsylvania) for providing the coals used in this bench-scale development program and to R. Kaplan of the Commercial Testing & Engineering Company (Chicago, Illinois) for his cooperation in expediting coal analyses for TRW.

METRIC CONVERSION FACTORS

In compliance with EPA policy, metric units have been used extensively in this report (followed by British units in parentheses). However, in some cases, British units have been used for ease of comprehension. For these cases, the following conversion table is provided:

British	Metric
1 Btu	252 calories
1 Btu	2.93×10^{-4} kilowatt-hours
1 kw	1,000 joules/sec
1 hp (electric)	746 joules/sec
1 psi	0.07 kilograms/cm^2
5/9 (°F-32)	°C
1 inch	2.54 centimeters
1 ft	0.3048 meter
1 ft^2	0.0929 $meters^2$
1 ft^3	0.0283 $meters^3$ or 28.3 liters
1 gallon	3.79 liters
1 pound	0.4536 kilograms
1 ton (short)	0.9072 metric tons

CONCLUSIONS

General Conclusions

1. The Meyers Process applied to high-ash run-of-mine coal is capable of removing in excess of 90 percent of the pyritic sulfur from 14 and 100 mesh top-size coal and at least 80 percent from coarser coal (1/4 inch top-size).*

2. Physical cleaning of coarse coal appears to enhance the pyrite leaching rates of the Meyers Process. Pyrite removals in excess of 90 percent were attained with cleaned 1/4 inch top-size Lower Kittanning coal.

3. Meyers Process operation under simultaneous coal leaching-reagent regeneration processing is feasible and efficient. It appears to be the most economic mode of processing high pyritic sulfur coal of at least up to 14 mesh top-size.

4. Simultaneous leaching-regeneration processing of coal up to at least 130°C and 150 psig (135 psi oxygen pressure) does not measurably affect the organic matrix of the coals tested.

5. Pyrite leaching rates are not affected by the quantity of coal present in the slurry. Processing of slurries containing up to at least 33 wt percent solids is feasible. Process coal throughput doubled and filtration time (cost) was reduced when the slurry solids concentration was upgraded from 20 to 33 wt. percent.

6. Solid-liquid separations of process slurries are feasible by commercially available equipment (vendor tests). The filtration costs of 14 mesh top-size coal slurries are approximately one-half those of 100 mesh top-size coal slurries while the difference in pyrite leaching rates is no more than 20 percent.

7. The process may be engineered in a number of basic design configurations including simultaneous leach and regeneration, separate leach and regeneration, use of oxygen or air for regeneration, fine coal or coarse coal processing, and in combination with coal cleaning; these process design schemes lead to stand-alone full capital cost estimates of $30-80/KW of power plant name capacity.

8. The estimated coal desulfurization costs, annualized on a utility financed basis, range between $0.33 and $0.51/MM Btu. Assuming ROM coal costs of $20/ton, the costs of the desulfurized fuel are estimated to range between $1.14 and $1.32/MM Btu.

---

*EPA policy is to express all data in Agency documents in metric units. For those particular non-metric units utilized in this report conversion factors have been provided. These factors are located on page xvii.

Specific Conclusions

1. The efficiency and selectivity of ferric sulfate solutions in the leaching of pyrite from coal observed during previous investigations[1] was reproduced in the current program with high ash (30 percent) Run-of-Mine Lower Kittanning (ROM L.K.) coal containing 4 percent pyritic sulfur. Eighty-three percent of the pyrite was removed from 100 mesh top-size L.K. coal during 8.5 hours of processing a 20 wt percent coal slurry at 102°C under ambient pressure.

2. The L-R processing (simultaneous coal leaching-reagent regeneration) scheme developed in this program led to substantial improvement in the rate of pyrite removal from fine coal, up to at least 14 mesh top-size, over that obtained under ambient pressure processing. Approximately eighty percent of the coal pyrite was removed in only two hours when 20 wt percent slurries of 100 mesh top-size L.K. coal were processed under L-R conditions at 120°C and 100 psig pressure (85 psi oxygen). The large improvement in pyrite leaching rates appears to be principally due to temperature increase. The rate advantage of L-R processing ceased to apply when pyrite removal exceeded approximately 80 percent.

3. The commercial scale processing scheme developed from bench-scale data for the desulfurization of high pyrite coal consists of the following unit operations connected in series: mixer, L-R reactor, ambient pressure reactor, coal-reagent separation, processed coal wash, coal-water separation, elemental sulfur recovery, and coal drying. All unit operations were successfully tested at bench-scale.

4. Pyrite removal occurs in the mixer, L-R reactor, and ambient pressure reactor. The removal rate in all three reactors is governed by the empirical leaching rate expression

$$r_L = -\frac{dW_p}{dt} = K_L W_p^2 Y^2,$$

where

W_p = wt percent pyrite in coal,

Y = ferric ion-to-total iron ratio in the reactor reagent, and,

K_L = rate constant, a function of temperature and coal top-size.

5. Up to approximately 80 percent pyrite removal, the rate constant shows a strong temperature dependence expressible by

$$K_L = A_L \exp(-E_L/RT)$$

Beyond 80 percent removal, the K_L value appears virtually unaffected by temperature in the range investigated (90°C to 130°C). Apparently, a change of reaction mechanism occurs when pyrite removal exceeds 80 percent; it is speculated that a diffusion controlled process takes over. This change in mechanism may be specific to this particular high-ash coal.

6. The E_L value is independent of temperature, coal top-size (up to 14 mesh), or reactor unit operation (processing conditions). The value of A_L is independent of temperature under mixer and L-R operations, but different for each operation. The reasons for this unexpected A_L value dependence on mode of operation are not apparent from the available data. The estimated E_L and A_L values for mixer and L-R reactor processing and those of the diffusion rate constant are summarized in the report.

7. Reagent regeneration is governed by the rate expression

$$r_R = -\frac{dFe^{+2}}{dt} = K_R P_{O_2}(Fe^{+2})^2,$$

where

$K_R = A_R \exp(-E_R/RT)$,

P_{O_2} = oxygen partial pressure, and

Fe^{+2} = ferrous ion concentration in the reagent solution.

A_R and E_R are constants.

The reagent regeneration rate operates simultaneously with the leaching rate in the L-R reactor.

8. The K_L value at 120°C under L-R processing conditions is five times higher than the K_L value for 102°C processing under ambient pressure conditions (separate leaching and regeneration); both the 14 and 100 mesh top-size coals exhibit the same large increase in K_L value. The estimated E_L justifies only a two-fold increase in K_L for 20 degree temperature rise-observed between 80° and 102°C (separate leaching-regeneration) and between 110° and 130° (L-R processing). The 250 percent increase in the K_L value, which appears to be the result of changing the mode of processing, could not be attributed to reaction of oxygen with pyrite.

Additional rate data of more fundamental nature are required to delineate the reasons for the unexplained increase in K_L.

9. The K_L value obtained with 100 mesh top-size L.K. coal was approximately 20 percent larger than the K_L obtained with 14 mesh top-size coal. Since solid-liquid separation efficiency increases substantially with coal top-size, it appears preferable to process 14 mesh coal in view of the small rate penalty involved.

10. The coal top-size effect on K_L becomes substantial with ROM coals coarser than 14 mesh top-size. The ratio of K_L values obtained at 102°C with 100 mesh and 1/4 inch top-size L.K. coals is estimated to be equal to 4 up to approximately 60 percent pyrite removal and between 6 and 9 for higher pyrite removal. L-R processing of coarse ROM coal at 120°C did not appear to improve the above ratios. In fact, in the case of 3/8 inch top-size ROM coal increasing the temperature from 102°C to 120°C has probably no effect on the leaching rate when pyrite removal exceeds 20-25 percent.

11. Despite the adverse effect of coal particle size on pyrite leaching rates, coarse ROM coal desulfurization by the Meyers Process is feasible. Pyrite reduction in excess of 80 percent was attained when 1/4 inch x 0 ROM L.K. coal was leached for 48 hours with ferric sulfate solution at 102°C. The pyritic sulfur content of the ROM coal was reduced from 3.48 wt. percent to 0.66 wt. percent and its heat content increased from 11,822 to 13,023 btu per pound.

12. Preliminary data on cleaned coarse coal processing by the Meyers Process indicate that physical cleaning of high pyrite ROM coal prior to chemical desulfurization enhances substantially the pyrite leaching rate. At 102°C, the pyrite leaching rate obtained from processing the 8 x 14 mesh fraction of cleaned L.K. coal was twice that obtained from processing the same size fraction of ROM L.K. coal. The pyritic sulfur content of the cleaned fraction was reduced from 1.06 to 0.09 wt. percent.

13. In addition to temperature and coal particle size, the K_L value may also be affected by the type or source of coal. Data obtained from the L-R processing of Marion mine coal (Upper Freeport coal) indicate that the pyrite leaching rate constant applicable to this coal is at least an order of magnitude higher than corresponding K_L values applicable to L.K. coal. This comparison assumes that the same leaching rate expression applies to both coals.

14. The concentration of coal in the slurry and the concentration of iron in the reagent affect the leaching rate through their effect on Y. These effects become negligible under continuous exchange or L-R processing. Thus, in principle, the coal content of the slurry is limited only by equipment limitations in the transfer of thick slurries and the iron content of the reagent is limited only by the solubility of the iron sulfate in water.

15. The sulfate sulfur-to-elemental sulfur ratio of the product sulfur of the Meyers Process is independent of the mode of processing or the value of the processing parameters used within the ranges investigated. The value of the ratio is approximately 1.5 indicating that 60 percent of the reacted pyritic sulfur converts to sulfate sulfur and 40 percent to elemental sulfur.

16. Elemental sulfur recovery is virtually complete by extraction of processed coal with toluene. However, preliminary data revealed that recovery by vaporization is also efficient. The latter scheme combines sulfur recovery and coal drying into a simple operation and, therefore, appears to be the more desirable method of sulfur recovery. Additional experimentation is needed in order to optimize sulfur product recovery techniques.

17. Special investigations revealed that the Meyers Process does not affect standard coal analysis techniques.

18. Experimentation with potential reactor construction materials for the Meyers Process revealed that 316L stainless steel could be safely used, but 304 stainless steel was inadequate.

19. Process analyses for both fine and coarse coal processing show that the reactor/regenerator section of the process accounts for a large part of the equipment cost. At commercial scale it was estimated that 40-60 percent of the total equipment cost occurs in this section.

20. All liquid streams of the Meyers Process are being recycled. Because of the closed loop design of the process, separate optimization of the reactor section generally leads to inoperable designs. The reactor trade-offs must be coupled to the wash and by-product recovery sections in all process optimization efforts.

21. The process analyses showed that either low purity oxygen (95%) or high purity oxygen (99.5%) could be used with no significant process cost impact. It also showed that air can be competitive if energy is efficiently recovered from the reactor vent gas. Air regeneration may be applicable only to high pyrite coals where the heat liberated by regeneration is sufficient to saturate the large volume of inert vent gas.

RECOMMENDATIONS

1. The principal unit operations of the Meyers Process are sufficiently developed at bench-scale to merit immediate scale-up to the pilot plant stage.

2. Bench-scale testing should continue in support of pilot plant testing for identification of process improvements and for the evaluation of process application to new areas or coals. Bench scale represents the most cost effective scale to investigate process improvements and expanded utility.

3. In support of pilot plant testing it is recommended that bench-scale data be generated to aid in coal selection and in test plan formulation best suited to each of the selected coals. Bench-scale investigations should also be used as an aid to understand and explain unexpected observations and to resolve problems that may occur.

4. In the area of process improvements, it is recommended that bench-scale investigations be performed on improved techniques for sulfur product recovery, on schemes for coal trace element recovery, on means of product utilization or disposal, and on the identification and preliminary evaluation of process modifications with the potential for reducing processing costs; e.g., simultaneous sulfate and elemental sulfur recovery and elimination of coal wash, combination of physical coal cleaning and chemical desulfurization.

5. In the area of expanded process utilization, bench-scale studies are recommended to investigate the feasbility of using the Meyers Process to render presently unusable coking coal acceptable to metallurgical industry (high sulfur coal, middlings) and to examine the advantages of combining chemical desulfurization with coal conversion. Simultaneous chemical desulfurization and non-pyrite ash reduction should also be investigated.

6. Coal pyrite leaching rate studies of more fundamental nature than previously performed are needed and recommended. These studies should aim at prediction of the efficiencies of chemical coal desulfurization from easily measured physical and/or chemical properties of coal. At a minimum, studies should be undertaken which identify the influence that the coal matrix exerts on coal pyrite leaching rates.

7. Process designs should be prepared for low pyrite coals to identify the ranges of parameters that should be included in the experimental investigations. Emphasis should be placed on the reactor/regenerator area which continues to be the major cost portion of the process.

1. INTRODUCTION

The Meyers Process can be used to desulfurize a large number of coals prior to combustion in order to meet govermental requirements for sulfur oxide emissions control.

The process consists of several steps including crushing, chemical treating, sulfur removal and solution regeneration. While the process is new, the unit operations are similar to various existing technologies such as processes for the heap leaching of copper, regeneration of steel mill waste pickle liquor and recovery of elemental sulfur from volcanic ash. The chemistry of the process is represented by the pyrite leaching and reagent regeneration steps shown below:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S$$

$$2.4\ O_2 + 9.6\ FeSO_4 + 4.8\ H_2SO_4 \rightarrow 4.8\ Fe_2(SO_4)_3 + 4.8\ H_2O$$

overall process reaction:

$$FeS_2 + 2.4\ O_2 \rightarrow 0.6\ FeSO_4 + 0.2\ Fe_2(SO_4)_3 + 0.8S$$

Generated iron sulfates can be recovered by crystallization and stabilized for disposal or a part of the iron sulfate product may be neutralized with lime to yield gypsum. For the processing of fine or suspendable coal (e.g., 14 mesh top size) leaching and regeneration are often economically combined in a single process unit, while for the processing of coarse coal (e.g., -3/8 inch) the two reactions are more economically performed separately.

The Meyers Process is more applicable to coals rich in pyritic sulfur rather than those in which organic sulfur is in high concentration. Such coal is found in the Appalachian region of the United States which now supplies 60 percent of the current U.S. production. An estimated one-third of the Appalachian production can be lowered to sulfur contents of 0.6 to 0.9 percent at which level the emission requirements for new power plants can be met. Additional Appalachian and Interior Basin coal can meet the state emission standards by this process.

An initial bench-scale testing program for the definition and obtaining of critical design data for the Meyers Process for the chemical removal of pyritic sulfur from coal was performed.[1] In addition, a survey program covering application of the process for desulfurization of pulverized, raw run-of-mine coal from 35 U.S. coal mines has been completed.[2,3] Run-of-mine coal was used in all of these experimentation in order to accentuate any possible processing difficulties which might be caused by the presence of unusually large concentrations of pyrite and inorganic ash. The effort demonstrated that the process, even when operating on ROM coal, has wide applicability for the reduction of sulfur content of U.S. coal to levels consistent with the Federal Standards for New Stationary Sources.

This bench-scale program was aimed at optimizing and improving the critical leaching and regeneration process steps, evaluating analytical procedures and studying other process improvements. As before, high ash run-of-mine coal was used for the majority of the experimentation, while studies aimed at determining the benefits of clean coal processing utilized coal typical of washed Appalachian coal.

This effort resulted in the attainment of the necessary data and definition of some significant improvements. In doing so, more than fifty fully material balanced process simulation runs, requiring approximately 2000 solution analyses and 1000 individual coal analyses, were performed. These data were assessed and evaluated in combination with the results reported in the initial bench-scale program.

The resulting report is necessarily extensive, and therefore a guide is provided to the reader who wishes to focus his attention on specific program results. The results in this volume are presented in six major sections as follows:

- Pyritic Sulfur Removal from Suspendable Coal
- Reagent Recyclability-Trace Element Data

- L-R Processing of Coarse Coal
- Process Engineering
- Chemical Analysis Studies
- Materials Compatibility

while the complete data base is presented in Volume II of this report.

Those readers desiring to review process unit operations for suspendable coal are directed to Sections 2.4 through 2.7 of this report. Those readers desiring process design, estimated process capital cost and estimated operating costs are directed to Sections 5.1 and 5.3. Coarse coal depyritization data and the engineering analysis for a coarse coal processing scheme are presented in Sections 4 and 5.2, respectively. Section 6 of the report is devoted to sulfur analysis techniques for processed coal and the identification of potential process monitoring techniques. Section 7 presents data on materials compatibility to process environment.

2. PYRITIC SULFUR REMOVAL FROM SUSPENDABLE COAL

The bulk of the program effort was expended in the processing of suspendable coal. Coal is defined here as suspendable if its top size does not exceed 10 mesh. Two coal sizes were investigated: 100 mesh x 0 and 14 mesh x 0. The emphasis in experimentation was placed in optimization of pressurized simultaneous coal leaching-reagent regeneration (L-R) processing and the parameters affecting this type of processing.

The ensuing report sections describe in detail the experimentation performed, the procedures used, the data generated, and our interpretation of the data.

2.1 COAL SELECTION AND SAMPLE PREPARATION

A Lower Kittanning coal seam feed was selected for the majority of experimentation on this program while the Upper Freeport Seams Sample was processed for comparison purposes. This selection was based on the availability of large deposits of these coals, the fact that a substantial data bank existed on ambient pressure processing of Lower Kittanning coal by the Meyers Process,[1] the availability of data on Upper Freeport coal from the coal survey project,[2] and the similarity of process behavior of these seams to most Appalachian coals.

Raw run-of-mine Lower Kittanning coal was ground to 3/8 inch x 0 size and shipped to TRW by the Bureau of Mines, Pittsburgh, Pennsylvania at the request of the EPA Project Officer. The coal was received in three 55-gallon drums with each drum containing approximately 150 kilograms of coal.

Preceding page blank

The coal from each drum, when needed for experimentation, was successively halved by the use of commercial rifflers to approximately 20 kilogram lots. This was the minimum lot size used for further grinding (100 mesh and 14 mesh top sizes). Upon grinding, each 20 kilogram lot was subjected to the same riffling procedure (halving) until the desired coal sample size was attained. The nominal coal sample sizes used in this program were 2 kilograms (20 wt. percent slurry processing) and 4 kilograms (33 wt. percent slurry processing). Samples submitted to analyses were in the 200 to 300 grams range. The described riffling procedure is the most commonly used method for coal sampling and it is ASTM approved (ASTM sampling analysis procedures utilized in this program are listed in Appendix G, Volume II). Both the "as received" and the unused portion of the ground coal were stored under helium in order to inhibit weathering. However, sulfur-forms analyses of the unprocessed coal performed periodically during the program indicated that some coal weathering took place in spite of the precautions taken (see Table 1).

The unprocessed coal was completely characterized prior to initiation of processing. The coal characterization procedure included complete coal analyses and coal particle size distribution determinations. The coal analyses involved short proximate (moisture, ash, and heat content), sulfur forms, ash composition, and trace element determinations. In addition, short proximate, sulfur forms, and ash-iron analyses were performed periodically on the unprocessed coal during the duration of the program in order to assure proper sampling and to monitor coal weathering. The coal analyses, with the exception of trace element analyses, were performed by Commercial Testing & Engineering Company (CT&E), Chicago, Illinois. The trace element analyses were performed by TRW's Applied Chemistry Department.

Table 1 summarizes the analysis data on the raw Lower Kittanning coal used in this program. The data are presented chronologically with respect to the dates of analysis in order to illustrate the increase in the sulfate content of the coal with storage time and the associated decrease in pyrite.

TABLE 1. RAW LOWER KITTANNING COAL ANALYSES

Date Analyzed	Coal Top Size	Number Of Samples Analyzed	Coal Composition, Dry							Moisture In Raw Coal (Wt.%)
			Ash (Wt.%)	Heat Content (Btu/Lb)	Total Sulfur (Wt.%)	Pyritic Sulfur (Wt.%)	Sulfate Sulfur (Wt.%)	Organic Sulfur (Wt.%)	Iron (Wt.%)	
Oct. 1973	100 Mesh	3	30.08 ±.02	10,520 ± 26	4.55 ±.03	4.05 ±.01	0.08 ±.02	0.41 ±.04	3.91 ±.03	1.20 ± 34
Dec. 1973	14 Mesh	2	29.76 ±.70	10,626 ± 173	4.48 ±.01	4.01 ±.01	0.07 ±.01	0.41 ±.01	4.03 ±.12	1.51 ±.03
April-June 1974	100 Mesh	4	30.85 **	10,275 **	4.53 ±.06	3.88 ±.19	0.24 ±.04	0.41 ±.17	3.98 ±.06	1.19 ±.22
May 1974	14 Mesh	2	32.32 ±.35	10,109 ± 106	4.77 ±.01	3.85 ±.02	0.28 ±.01	0.64 ±.01	4.20 ±.04	1.81
June 1974	14 Mesh	1	30.12	10,324	4.50	3.85	0.26	0.39	3.89	1.23
Sept. 1974	3/8 inch*	3	28.91 ±.52	10,448 ± 106	4.28 ± 14	3.56 ± 18	0.35 ±.03	0.37 ±.03	3.68 ±.13	1.16 ±.04
Oct. 1974	14 Mesh	4	31.77 ±.71	10,020 ± 77	4.55 ±.07	3.77 ±.04	0.41 ±.02	0.38 ±.05	4.00 ±.09	1.66 ±.19

*These samples were taken from a different drum than the rest.

**Single analysis.

The observed trend with time in the values of these two sulfur forms, the internal consistency in individual sample analyses (each increase in sulfate is associated with a corresponding decrease in pyrite), and the good agreement in the total sulfur and iron values among coal samples derived from different ground lots and analyzed at different times indicate that the variations in pyritic and sulfate sulfur from sample to sample are not due to sampling or analysis error but to coal weathering. With one exception, the data in Table 1 verify the adequacy of raw coal sampling procedures used by TRW and the consistency in analyses performed at CT&E. The indicated standard deviations are within ASTM standards.

The exception to the overall consistency of data in Table 1 involves the two samples of 14 mesh x 0 coal analyzed in May 1974. The higher ash, lower heat content, higher total sulfur, and higher iron values of these samples (compared to the rest of the data on coal derived from the same drum) would be internally consistent and would indicate inappropriate sampling if the analyzed higher total sulfur was due to higher inorganic sulfur forms in the sample (higher inorganic sulfur leads to higher ash and lower heat content in the sample). However, the sulfur forms data from these two samples show that the unexpected high total sulfur content was due to high organic sulfur. This analysis is not consistent with the higher iron and ash content of the samples which suggest that the pyrite or iron sulfate forms should have exhibited the high values. Thus, in addition to sampling procedure the sample analyses became suscept. The same lot of ground coal was re-sampled and reanalyzed in June and yielded the expected values (Table 1).

Discrepancies in sulfur forms analyses were more frequent with processed coal. The low sulfur-high ash content of the processed coal and/or residual elemental sulfur left on the coal during processing could have been the culprits of poor sample analysis. Whenever these discrepancies occurred, the coal sample analysis data were subjected to the same internal consistency scrutiny as that described for the raw coal.

Table 2 presents the data on the mineral content of the coal utilized (ash composition). These data were supplemented with trace element analyses; the latter are presented in a later section of this report devoted exclusively to the fate of trace elements during coal processing. The ash composition data appears to be typical of Pennsylvania bituminous coals (the quantity of ash in the coal was not typical; its softening temperature was 1385°C (2525°F)).

TABLE 2. LOWER KITTANNING COAL ASH COMPOSITION

Ash Component	Wt. %
Phos. pentoxide, P_2O_5	0.11
Silica, SiO_2	49.63
Ferric oxide, Fe_2O_3	18.66
Alumina, Al_2O_3	25.64
Titania, TiO_2	1.87
Lime, CaO	0.75
Magnesia, MgO	0.53
Sulfur trioxide, SO_3	0.79
Potassium oxide, K_2O	1.64
Sodium oxide, Na_2O	0.29
Undetermined	0.09
	100.00

Table 3 presents data on the particle size distribution of the received 3/8 inch x 0 coal and of the two suspendable coal sizes investigated in this program (14 mesh x 0, and 100 mesh x 0). At least three determinations were performed on each of the coal top sizes; the sample to sample reproducibility was very good. The particle size distribution presented in Table 3 proved to be almost identical to that obtained from the Lower Kittanning coal used in the previous program (EPA contract EHSD 71-7).[1]

TABLE 3. LOWER KITTANNING COAL PARTICLE SIZE DISTRIBUTION

Size Range	Weight Fractions*		
(Mesh)	100 Mesh x 0	14 Mesh x 0	3/8 Inch x 0
+6			.248
-6 +14		.020	.260
-14 +28		.200	.150
-28 +42		.160	.093
-42 +60		.090	.054
-60 +80		.080	.038
-80 +100	.090	.040	.018
-100 +115	.051	.040	.019
-115 +150	.054	.030	.013
-150 +200	.136	.100	.026
-200 +325	.592	.210	.054
-325 x0	.071	.020	.021
Lost	.006	.010	.006

*Three sample averages (maximum deviation 10%)

Coal grinding and riffling to the desired sample size for processing (2 to 4 kilograms) were the only operations performed on the coal prior to mixing it with the reagent for processing. Thus, the data generated on this program was on ground run-of-the mine coal.

2.2 COAL PROCESSING EXPERIMENTATION

As a result of previous bench-scale investigations on the Meyers Process, a conceptual process scheme was proposed, for processing suspendable coal, involving the following basic unit operations: slurry preparation (mixer), simultaneous coal leaching-reagent regeneration (L-R reactor), ambient pressure residual pyrite leaching-coal settling (settler), coal washing, elemental sulfur recovery, coal drying, and product sulfate recovery. The major objective of the current program was to investigate the validity of the above conceptual scheme. The principal difference between the above scheme and the one defined in the previous bench-scale program is L-R processing (simultaneous leaching-regeneration under pressure versus separate coal leaching and reagent regeneration unit operations with coal leached at ambient pressure). Thus, the emphasis was placed on L-R processing; however, its effects on the other unit operations as well as potential improvements on these operations were also investigated. The investigation of product sulfate recovery (process slip-stream treatment) was postponed until the basic process parameters are finalized (especially reagent composition). Preliminary examination of this unit operation has been proposed to commence at the conclusion of this program.

Figure 1 is a block diagram of the basic processing scheme used in the investigations of suspendable coal. Every effort was made to simulate the envisioned full-scale processing to the degree allowable by the size of bench-scale equipment. Figure 2 depicts in greater detail the front end of the process and the apparatus utilized (mixer, L-R reactor, and settler). The ensuing paragraphs describe the procedure and the equipment used.

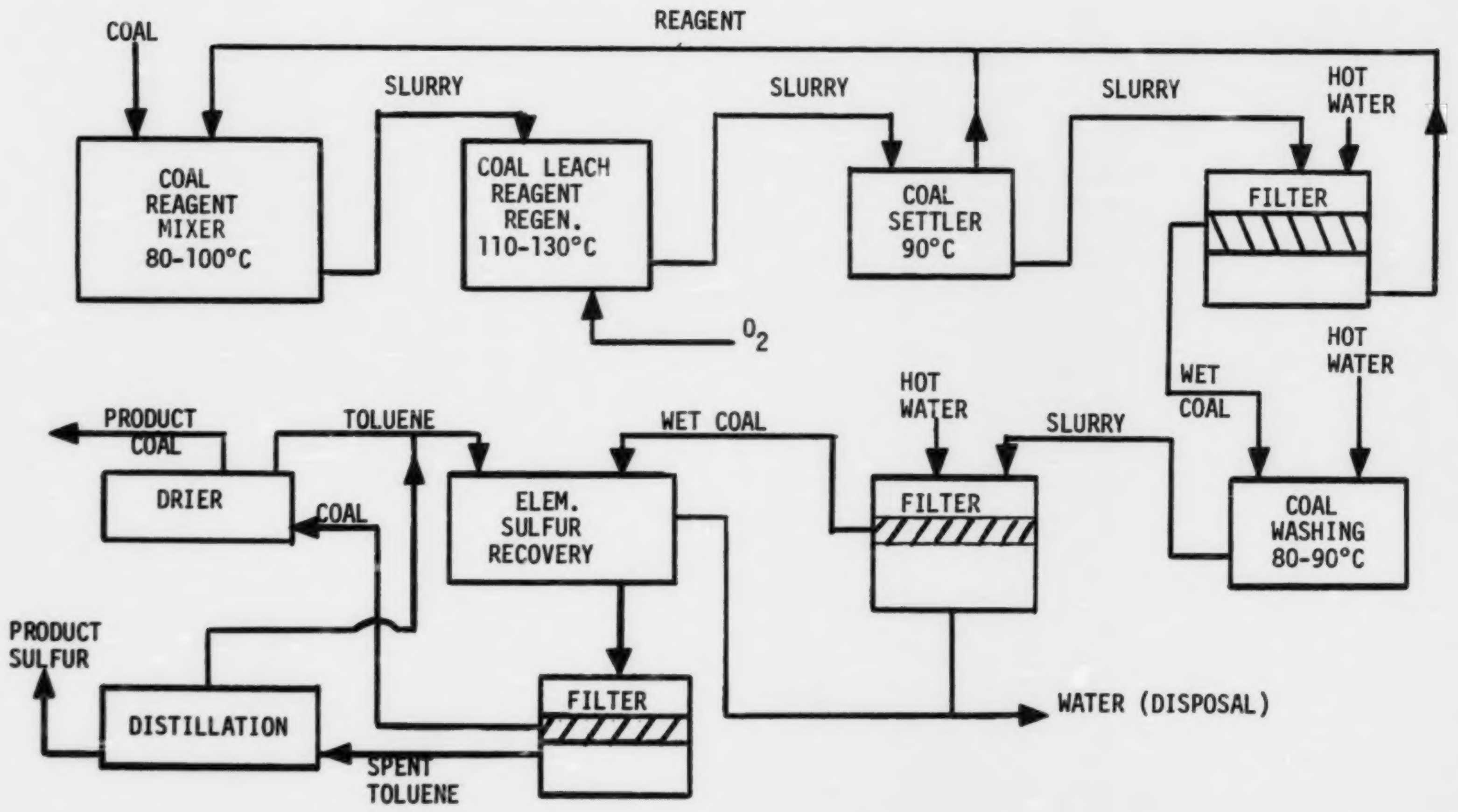
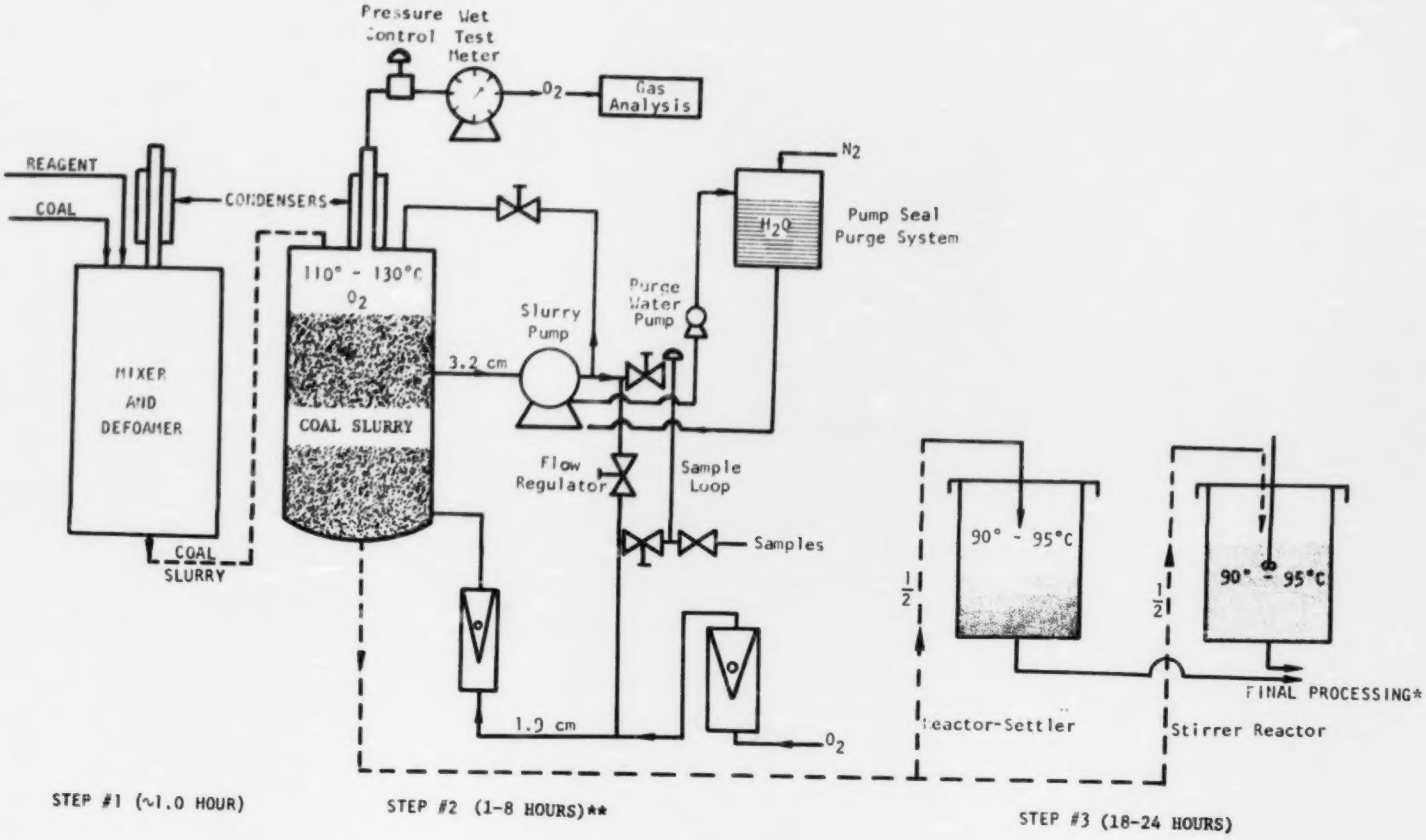

COAL
REAGENT
SLURRY
SLURRY
SLURRY
HOT WATER
COAL REAGENT MIXER 80-100°C
COAL LEACH REAGENT REGEN. 110-130°C
COAL SETTLER 90°C
FILTER
O_2
HOT WATER
WET COAL
PRODUCT COAL
TOLUENE
WET COAL
HOT WATER
SLURRY
DRIER
COAL
ELEM. SULFUR RECOVERY
FILTER
COAL WASHING 80-90°C
PRODUCT SULFUR
DISTILLATION
FILTER
WATER (DISPOSAL)
SPENT TOLUENE

Figure 1. Basic Bench-Scale Processing Scheme for the Removal of Pyritic Sulfur From Coal


Pressure Control
Wet Test Meter
O_2
Gas Analysis
REAGENT
COAL
CONDENSERS
N_2
H_2O
Pump Seal Purge System
MIXER AND DEFOAMER
110° - 130°C
O_2
COAL SLURRY
Slurry Pump
3.2 cm
Purge Water Pump
Flow Regulator
Sample Loop
Samples
COAL SLURRY
1.9 cm
O_2
1/2
90° - 95°C
Reactor-Settler
1/2
90° - 95°C
Stirrer Reactor
FINAL PROCESSING*
STEP #1 (~1.0 HOUR)
STEP #2 (1-8 HOURS)**
STEP #3 (18-24 HOURS)

---

*Final processing includes elemental sulfur recovery, coal washing and drying.

**Reactor volume ~13 liters

Figure 2. Bench-Scale Coal Leaching and Reagent Regeneration Apparatus

The ground coal (14 or 100 mesh top size) was mixed with hot spent or fresh reagent in the "mixer" and the resulting slurry was brought to boiling; slurry boiling was maintained until coal wetting was complete (slurry foaming subsided). Actually, the "mixer" was comprised of 3 to 4 four-liter glass flasks equipped with heating tape and stirrer; each flask contained approximately 2 liters of slurry. The "defoamed" slurry was then transferred to the L-R reactor; the reactor was pressurized with nitrogen gas to the desired operating pressure (50 to 150 psig) and the slurry was heated to the desired L-R temperature (110 to 130°C). This entire "slurry preparation and heating" operation ("mixer operation") required approximately one hour (mixing time, t_m), although in early experimentation it was substantially longer. Once the desired L-R temperature was reached, a slurry sample was taken and then oxygen was introduced to the reactor. The composition of the slurry sample taken at this point (t_{L-R} = 0.0 hours) defined the starting coal and reagent composition of L-R processing and simultaneously served as the means of determining the extent of reaction during t_m.

The L-R reactor and its associated parts (feed and sampling lines, pump, and slurry circulation loops) were constructed from 316 stainless steel stock. The reactor was a cylinder 100 cm (39.4 inches) in length with a 14 cm (5.5 inches) OD and 12.7 cm (5.0 inches) ID. The reactor was flanged at the one end (top) and a hemispherical bottom was welded to the other end. Both end pieces were equipped with 2.54 cm (1 inch) openings.

The reactor was loaded with slurry through the top and drained through a one inch ball valve attached to the reactor bottom. The reactor was operated one-half to three-quarters full.

During L-R processing the slurry was circulated through a loop external to the reactor (Figure 2) at a rate of approximately 4 liters per minute. Slurry circulation was necessary for oxygen introduction and for sampling. Slurry was circulated with the aid of a 316 stainless steel centrifugal pump having a 3.2 cm (1.25 inches) OD suction and an 1.9 cm

(0.75 inches) OD discharge. The pump was equipped with a water irrigated double mechanical seal. The slurry was withdrawn from a reactor opening located 30 cm from its bottom and, after oxygenation, it was returned through a tangential inlet to the reactor bottom. The main circulation loop was equipped with two by-pass loops. One was used to trap slurry samples at the desired reaction times. The second was used to return part of the oxygen depleted slurry through the top of the reactor as a spray. The principal function of the second by-pass was to control flow through the main loop without the need of excessive throttling of the pump; an intended second function during early experimentation was slurry foam control. However, top spraying the reactor slurry did not prove to be a very effective foam control device). This by-pass loop was assembled from a variety of stainless steel tubing and as such it also served as a means of testing the compatibility of these materials with L-R processing (the materials involved and the data derived from these tests are decribed in a separate section of this report).

Oxygen was introduced to the slurry immediately downstream of the sample trap at a rate which varied from approximately 0.5 to 2.0 liters* per minute; the oxygen feed rate depended on the quantity of coal being processed and on L-R processing time (higher rates were fed at the start of L-R to purge the nitrogen in the reactor and to accommodate the higher reaction rates). In principle, due to the prevailing turbulent flow conditions, intimate gas-slurry mixing took place in the recirculation loop prior to slurry return to the reactor. The excess oxygen, oxygen not consumed by reagent regeneration, percolated through the reactor, passed through a condenser which removed water vapor and entrained reagent solution, and exited the reactor through an automatic pressure relief valve. The quantity of reactor vent gas (principally oxygen) was measured by a wet-test meter.

Several slurry samples were taken during L-R processing (normally every 0.5 hours during the first two hours of processing and every hour thereafter). The drawn slurry samples were weighed and immediately filtered. The filtrate was analyzed for iron forms (Fe^{+2} and Fe^{+3}). The reagent wet coal was spray-washed with hot water to remove the reagent solution from it, extracted in toluene to leach out elemental sulfur, dried at 100°C under vacuum, and weighed. The weight percents solids in the slurry samples were determined and compared to the starting values as a means of evaluating how representative the samples were of the reactor mixture. The dry coal samples were analyzed for ash, heat content, total sulfur, sulfur forms, and iron.

---

*At Standard Temperature and Pressure (STP).

After the desired L-R processing time was completed, the reactor was depressurized and drained. The L-R slurry was transferred immediately to either a "settler" for further reaction or to the filtration apparatus or to both. In all cases, because of equipment size restrictions, the slurry was processed through the post L-R operations in two batches. Three processing options were used: (a) both batches were "settler" processed prior to filtration, washing, elemental sulfur recovery, and drying; (b) only one of the batches (approximately one-half of the L-R slurry) was "settler" processed prior to further processing; or (c) neither batch was "settler" processed. In addition, there were two options in "settler" processing: (a) reaction in an agitated "settler" or (b) reaction in a non-agitated "settler". Whatever the option used, slurry processing through the remaining operations was the same. (There were a few exceptions where L-R processed coal was used for special experimentation in washing and elemental sulfur recovery operations; these will be noted as they occur in data presentation.)

"Settler" processing was conceived as a means of concentrating dilute L-R slurries of fine coal while simultaneously removing the last few percent of pyrite from L-R processed coal. Since it was realized that a relatively quiescent reactor could be subject to reagent concentration gradients and a consequent reduction in the pyrite leaching rate, an agitated "settler" was also used in parallel for comparison. Indeed, the non-agitated "settler" was not as effective a pyrite leaching reactor as the agitated one because of reactant and product segregation. The non-agitated settler was abandoned, during early experimentation, not because of reagent segregation problems but because L-R processing of thick slurries proved efficient and a thickener was judged unnecessary. The agitated "settler" was retained as an ambient pressure reactor where the slow reacting, last few percent of pyrite could be leached out of coal. Thus, in the majority of experimentation one-half of the L-R slurry was processed through an agitated settler and the other half was transferred directly to the filtration and washing unit operations. The coal derived from these two slurries (after washing, toluene extraction, and drying) was used to determine L-R processing and "settler" processing efficiencies.

The "settlers", covered 5-liter cylindrical glass vessels, were equipped with heating tapes, condenser, and stirrer (used only for agitated "settler" processing). The slurry was processed in these vessels for 18-24 hours at 90°C and at ambient pressure. Each settler was sampled at the start and at the end of processing. The slurry samples were analyzed for iron forms only.

The hot slurries from either the L-R reactor or "settler" were vacuum filtered. The reagent-wet coal was subjected to a 2 stage washing scheme with both stages consisting of the following: a slurry wash with a quantity of water equal to from 2 to 4 times the weight of dry coal estimated to be in the filter cake; a cake wash with two dry coal weights of water. The slurry washes were performed at reflux temperatures for 30 minutes. Additional water washing or coal washing with 0.1 N sulfuric was performed on processed coals whose analysis indicated excessive iron sulfate deposition. All filtrates were analyzed for iron forms.

The product elemental sulfur was extracted from the processed coal with toluene (special experimentation was also performed with hexane). The water-wet coal filter cake from the wash section was slurried in twice the estimated dry coal weight of toluene. The slurry was heated to the toluene-water azeotrope temperature (85°C) where it was maintained until the water in the slurry (from the wet cake) was distilled-off (the toluene was returned to the slurry continuously during distillation); the slurry was then refluxed for 30 minutes at its reflux temperature (108°C). Subsequently, the slurry was filtered hot and the resulting coal cake was rinsed with a small quantity of fresh toluene. The elemental sulfur in the toluene filtrate was recovered as a residue upon vaporization of the toluene. The toluene residue contained small quantities of dissolved coal along with the elemental sulfur. Each residue was analyzed (in triplicate) for sulfur. In the majority of experiments a double toluene extraction was performed.

The toluene-wet coal was vacuum dried in a well trapped oven. The dried processed coal was then sampled for analysis. Each batch of processed coal was subjected to short proximate, sulfur forms, and iron analyses.

The procedure described was the one followed with the majority of coal processing experiments. There was, however, special experimentation performed which involved single unit operations. These special requirements are described in conjunction with the data presentation.

2.3 COAL PROCESSING DATA

Approximately 50 batches of suspendable (100 and 14 mesh top size) Lower Kittanning coal were subjected to L-R processing (simultaneous coal leaching-reagent regeneration processing) during the feasibility and parametric investigations of the L-R mode of operation of the Meyers Process. The following parametric effects were investigated over the ranges indicated:

- Reaction time (Mixer, 1-2 hours; L-R, 1-8 hours; Settler, 18-24 hours)
- Slurry concentration (20 wt. percent and 33 wt. percent coal in iron sulfate)
- Starting reagent iron concentration (near 0.0 to 5 wt. percent)
- L-R reaction temperature (110°C to 130°C)
- L-R reaction pressure (50 to 150 psig, with a corresponding oxygen partial pressure variation of 35 to 135 psia)

- pH (1.4 to 1.9); actually, this was an investigation of the effect of sulfuric acid on L-R processing.

Special experimentation was performed in the following areas: ambient pressure desulfurization of the Lower Kittanning coal by continuous reagent exchange, slurry foam control, elemental sulfur recovery, coal washing, solids-liquid separations, and reagent recyclability.

It should be noted that the major objective of this program was to test the feasibility of conceptual Meyers Process improvements and to determine the processing scheme and operating parameters of the improved process. Thus, the parametric investigations were limited to ranges considered as the most economically and technically practical for process utilization. The number of parameter values investigated were limited to the minimum necessary to (1) identify trends, (2) establish the most probable parameter values for use in the process design and (3) develop empirical rate expressions which adequately describe coal pyrite extraction under the L-R mode of operation of the Meyers Process.

The processing data is summarized in the 15 tables of Appendices A, and C of this report (Volume 2). Appendix A includes the data derived from processing 100 mesh top size coal; Appendix B includes the 14 mesh top size coal data; and Appendix C presents the data derived from L-R processing of weathered coal with low-iron reagent (the starting reagent does not contain iron; it derives iron from coal during slurry preparation and processing). The experiments are numbered consecutively starting with Appendix A through Appendix C. To a large degree, the numerical order of the experiments corresponds with the order in which they were performed. Each table contains experiments (usually more than one) performed under the set of nominal conditions indicated in its title. Specific conditions pertaining to individual experiments are included with the rate data derived from the particular experiment. Two types of data are presented for each experiment: rate data, indicating the change in slurry and coal composition as a function of reaction time, and mass balance data, showing the overall process balance for solids, liquids, sulfur, and iron. Examples of the data presented in Appendices A through C and table explanations are given below.

Table 4 presents the rate data derived from Experiment 1. The coal was processed under the conditions indicated and in accordance with the procedure described in the previous section (Section 2.2). The first row of data indicate the actual coal (solids) content of the slurry (as opposed to the nominal or intended value used in the table title), the Y value of the starting reagent (the ferric ion to total iron ratio in the reagent), and the composition of the starting coal on dry coal basis. The next five rows present data derived from slurry samples (150-200 grams each) drawn from the L-R reactor during processing.

The first column of data in Table 4 indicates the L-R reaction times (t_{L-R}) at which samples were drawn. It also shows the time, t_m, required to mix the slurry (to thoroughly wet the coal in order to minimize slurry foaming) and to heat it to the desired L-R reaction temperature, 120°C in this case. A sample was always drawn at the start of L-R processing (end of "mixer operation"); a slurry sample was also drawn at the conclusion of L-R operation (t_{L-R}= 2 hours, in this case). The second column shows the solids content of the slurry samples; this data served as an indication of the adequacy of the sampling procedure. As seen, the solids content of each sample is nearly identical to that of the starting slurry. The third column shows the reagent Y value of the liquid phase of each sample as determined from iron forms analyses. Columns four through ten present the analyzed dry coal composition data for each of the slurry samples. The last two columns show the computed pyritic sulfur, S_p, removal from coal as a function of reaction time. Pyritic sulfur removal values were computed from coal sulfur forms analysis data; the S_p removal during t_m was also computed from ferrous ion production data.

The removal values "Based on Analyzed S_p" were computed from the differences in the pyritic sulfur content of the starting coal and that of the particular sample; the S_p values were determined from coal sample

TABLE 4. RATE DATA ON L-R PROCESSING OF 100 MESH TOP SIZE L.K. COAL WITH 3 WT. % IRON SOLUTION AT 120°C AND 100 PSIG (85 PSI O_2). NOMINAL SLURRY SOLIDS 20 WT. %

RATE DATA

EXPERIMENT NO. 1: t_m = 1.5 Hours, t_{L-R} = 2 Hours; t_s = 0; Fe in Starting Reagent = 2.98 Wt. %; Starting Y = 1.0

Reaction Time, Hours (t_m = time in mixer; t_{L-R} = time under L-R processing; t_s = time in settler)	Sample Slurry Composition		Coal Composition Wt. % (Except Heat Content), Dry							% S_p Removal	
	Wt. % Solids	Y (Fe^{+3}/Fe)	Ash	Heat Content, Btu/Lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron, Fe	Based on Analyzed S_p	Based on Corrected S_p
Starting Coal (5 Sample Average) and Slurry	18.9	1.0	29.62 ±.66	10,573 ± 91	4.52 ±.05	4.03 ±.03	0.08 ±.02	0.41 ±.04	3.97 ±.12		
Reactor Samples											
t_{L-R} = 0.0 Hours (t_m = 1.5 Hours)	18.6	.28	26.52	11,059	2.95	2.07 (3.09)*	0.29	0.59	2.74	49 (25)*	45?
t_{L-R} = 0.5 Hours	17.7	.58	24.95	11,172	2.42	1.52	0.42	0.48	2.60	62	61
= 1.0 Hour	N.A.	.75	28.05	10,310	2.25	1.17	0.82	0.26	3.10	71	75
= 1.5 Hours	19.0	.84	27.76	10,104	2.58	0.45	1.09	1.04	3.55	89	74
= 2.0 Hours	18.5	.84	27.89	9,974	2.23	0.49	1.39	0.35	4.04	88	90
Processed Coal Composition											
L-R Processed Coal { Batch A Batch B			30.60 26.22	10,179 10,993	2.00 1.46	0.15 0.08	0.32 0.31	1.53 1.07	3.64 3.17	96 98	69 82 } 76
Reanalyzed Sample (Batch A + B)			25.93	11,090	1.65	0.67	0.18	0.79	1.33	83	74

* Coal S_p content and % S_p removal based on FE2 (ferrous ion) production during t_m.

analyses performed at CT&E (Commercial Testing & Engineering Laboratories). Thus,

$$\% \; S_p \text{ Removal} = \frac{\% \; S_p \text{ (starting coal)} - \% \; S_p \text{ (sample)}}{\% \; S_p \text{ (starting coal)}} \times 100 \qquad (1)$$

This method of computation assumes that the weight of the coal remains constant during the reaction. This, of course, is not the case because of ash (pyrite) dissolution, but the error introduced in the above computation is insignificant (less than one percent error in the calculated removal).

The pyrite removal values "Based on Corrected S_p" were computed the same way except that an adjusted sample S_p value was used instead of that derived from coal pyrite analysis. The adjusted or corrected sample S_p value was computed as follows:

$$S_p \text{ (corr.)} = S_p \text{ (Anal.)} + S_o \text{ (Anal.)} - 0.43 \qquad (2)$$

The above correction is based on the following assumptions. First, the organic sulfur content (wt. percent) of the coal, S_o, was not affected by the Meyers Process and that its value will change only because of changes in the weight of the coal (ash dissolution). For the coal used in this program, this assumption fixes the coal S_o range during processing between 0.41 and 0.44 weight percent (0.43 was selected as the "expected S_o" for all samples in order to reduce the computations involved; the introduced error is insignificant). Second, the analyzed values for total sulfur, S_t, and sulfate sulfur, S_s, are correct; and third, the elemental sulfur produced during the process was completely recovered.

Experimentation performed to date has shown that the Meyers Process does not affect the S_o content in the coal other than through changes in coal weight because of ash dissolution. However, the S_o value is determined indirectly from S_t, S_p, and S_s analyses ($S_o = S_t - S_p - S_s - S_n$) under the assumption that the unrecovered product elemental sulfur in processed coal, S_n is virtually zero. Thus, the accuracy of the S_o value depends on the accuracy of S_t, S_p, and S_s analyses and the completness of S_n recovery. Equation 2, above, assumes that meaningful errors affecting S_o determinations occurred only in S_p analyses. Based on available data this assumption appears to be statistically valid for the following reasons: S_t and S_s analyses performed on the same sample consistently agreed within ± 0.05 or better; abnormalities in S_o determinations were observed at both high and low (near zero) S_s values; unrecovered S_n can not account for S_o values below 0.43 wt percent. A more direct proof of the validity of Equation 2 can be derived from the smoothing effect its application had on S_p removal rate data. It should be emphasized, however, that application of Equation 2 to every S_p value may not have been warranted; it was employed only for the sake of consistency (occasional erroneous application of Equation 2 does not affect conclusions drawn on the performance of the Meyers Process).

The last row of information in Table 4 presents data on the composition of the processed coal. In this particular experiment the coal was not "settler" processed; the L-R slurry was processed in two batches through the rest of the unit operations (filtration, washing, elemental sulfur recovery, and drying) because of equipment size limitations. Thus, in principle, the two-hours reactor sample and the samples from Batches A and B should have been of the same composition (identically processed coals). Obviously they were not. Even though a part of the discrepancy could be attributed to sulfur forms analysis errors, poor sampling appeared to also be responsible. The two batches of L-R processed coal were mixed, refluxed for 30 minutes in 0.1N H_2SO_4, dried, sampled, and analyzed (washing with acid was performed to remove deposited iron and sulfate sulfur thought to interfere with the accuracy of analysis). The "corrected S_p" value of the combined batch agreed well with the average of the "corrected S_p" values of the individual batches, but not with the two-hour reaction sample.

A coal sampling problem appears to be responsible for the discrepancy in the two S_p values of the starting L-R coal (t_{L-R} = 0.0 sample). The top value (2.07 wt. percent) was obtained from sulfur forms analysis of the coal in the drawn slurry sample. The value in parenthesis was computed from the measured quantity of ferrous ion produced during t_m. According to Meyers Process chemistry, repeatedly verified, 10.2 moles of Fe^{+2} are produced per mole of pyrite oxidized. Fe^{+2} production from side reactions of

Fe^{+3} with the organic matrix of the Lower Kittanning coal or with non-pyritic ash components is negligible. Since at t_m Fe^{+3} is not being regenerated dur to lack of oxygen, Fe^{+2} production is an accurate measure of pyrite removal from coal in the mixer (t_m reaction time). Thus, the S_p value in parenthesis and the corresponding S_p removal value were assumed to be the correct values. The discrepancy between the directly analyzed and Fe^{+2} computed S_p values have been attributed to poor reactor sampling at $t_{L-R} = 0.0$. Because of inadequate slurry mixing during the start of L-R operation, the sample drawn from the circulation loop contained the smaller particle size coal representing the coal fraction with higher pyrite depletion. Later reactor samples were substantially more representative of the coal in the reactor.

Early in the program we experienced difficulties in obtaining representative slurry samples (partially due to slurry foaming) and as a consequence the decision was made not to rely completely on reactor samples for the determination of S_p removal rates as a function of reaction time. Thus, separate experiments were performed for a number of L-R times, t_{L-R}, ranging from one to eight hours. This decision greatly expanded the planned experimental effort, but it also greatly improved data reliability. Alleviation of foaming problems and improved sampling procedures resulted in more representative samples as a scan of the data in Volume 2 and the data in Table 5 (Experiment 7) below indicate. However, sampling, even of processed dry coal, was not completely consistent. At least in part, the sampling difficulties can be attributed to the unusually high ash content of the coal utilized.

Table 5 is identical in format to Table 4 except that it includes the composition of "settler" processed coal (last row of Table 5). Settler processing, described in the previous section, was always conducted at 90°C. The coal slurry residence time in the settler in hours is indicated by the t_s value in parentheses. The "AG" notation indicates that the "settler" was stirred ("NAG" was used to denote quiescent "settler" processing). The difference in the S_p removal values between "L-R Processed Coal" and "L-R + Settler Processed Coal" represents the percent of starting coal pyrite removed during "settler" processing.

TABLE 5. RATE DATA ON L-R PROCESSING OF 100 MESH TOP SIZE L.K. COAL WITH 5 WT. % IRON SOLUTION AT 120°C AND 100 PSIG

RATE DATA

EXPERIMENT NO. 7: t_m = 1.0 Hour, t_{L-R} = 1.0 Hour, t_s = 19 Hours (~50% of Coal); FET (Iron in Reagent) = 4.94 Wt. %; Starting Y (Fe^{+3}/FET) = 0.95											
Reaction Time, Hours (t_m = time in mixer; t_{L-R} = time under L-R processing; t_s = time in settler)	Sample Slurry Composition		Coal Composition Wt. % (Except Heat Content), Dry							% S_p Removal	
	Wt. % Solids	Y (Fe^{+3}/Fe)	Ash	Heat Content Btu/Lb	Total Sulfur, S_t	Pyritic Sulfur, S_p	Sulfate Sulfur, S_s	Organic Sulfur, S_o	Iron, Fe	Based on Analyzed S_p	Based on Corrected S_p
Starting Coal (5 Sample Average) and Slurry	19.2	.95	30.85 ±.46	10,275 ± 60	4.53 ±.06	3.88 ±.09	0.24 ±.04	0.41 ±.07	3.98 ±.06		
Reactor Samples											
t_{L-R} = 0.0 Hours (t_m = 1.0 Hour)	20.2	.54	28.97	10,558	3.68	3.12 (3.01)*	0.19	0.37	3.14	20 (24)*	21
t_{L-R} = 0.5 Hours	20.4	.72	27.14	10,823	2.77	2.22	0.25	0.30	2.41	43	46
= 1.0 Hour	19.1	.88	25.15	11,147	1.75	1.04	0.29	0.42	1.57	73	73
Processed Coal Composition											
L-R Processed Coal			28.55	10,831	1.98	1.43	0.23	0.32	1.88	63	66
L-R + "Settler" (AG) Proc. Coal (t_s = 19)			25.64	11,072	1.21	0.49	0.27	0.45	1.25	87	87

* Coal S_p content and % S_p removal based on FE2 (ferrous ion) production during t_m.

Table 6 presents "Process Mass Balance" data from Experiment 1. The solids, liquids, sulfur, and iron overall process mass balances are summarized in separate sections of the table. The table is a computer print out summary of individual process unit operations. A mass balance computer program was written which utilized detailed information on the composition of feed and output streams (weights and analysis data) from each process unit operation of each experiment, performed the mass balance calculations on solids, liquids, and slurries around each unit operation (mixer, L-R reactor, settler, wash, elemental sulfur recovery leacher, and coal drier), and compiled the data on overall process mass balance shown in Table 6.

The "solids balance" in Table 6 refers to coal. The "input" and "dry process coals" (completely processed coal plus samples) are direct weight measurements (the moisture content of the feed coal was estimated from short-proximate analyses performed on the "as received" raw coal; it averaged very nearly one weight percent). The processed coal and samples were corrected for deposited reagent. The quantity of deposited reagent was estimated from the iron and sulfate sulfur analyses of the starting and processed coals (including samples) and from the extent of pyrite removal (S_p analyses). The excess iron on the processed coal (reagent derived iron) was assumed to be $FeSO_4$ and Fe_2O_3. For the majority of experiments this correction was small (little, if any, reagent deposition that withstood washing). The dissolved coal mineral matter was determined from starting and processed coal ash analyses converted to mineral matter (assuming the ash to be Fe_2O_3 and the mineral matter FeS_2); it is shown in Table 6 as "pyrite dissolved" and as "non-pyritic ash dissolved". The first quantity was determined from S_p coal analyses and the second by difference. Table 6 indicates that 3 grams of "non-pyritic ash" was deposited on coal during processing. This is probably due to normal ash analysis uncertainty (deviations). A scan of the data from all experiments indicates that a very small quantity of non-pyritic mineral matter was dissolved during processing. The "coal dissolved in solvent" (elemental sulfur recovery unit) was determined from the weight and sulfur content of the residue derived from the distillation of the spent organic solvent (toluene or hexane, toluene in the large majority of experiments).

TABLE 6. PROCESS MASS BALANCE DATA

Exp. 1, L.K.100X0MESH, 20PCT SLURRY(NOMINAL), 120C, 100PSIG(85PSI O2)

OVERALL SOLIDS BALANCE	
DRY COAL INPUT	1882
DRY PROCESS COALS(CORR. FOR DEP. REAG.)	1773
PYRITE DISSOLVED DURING REACTION	111
ASH(NON-PYRITIC) DISSOLVED DURING REACTION	-15
COAL DISSOLVED IN SOLVENT	3
TOTAL SOLIDS RECOVERED	1872
LOSS (INPUT - RECOVERED)	10
PERCENT RECOVERY OF SOLIDS	99

OVERALL COAL SULFUR BALANCE	
INPUT COAL SULFUR	85
PROCESS COAL SULFUR(CORR. FOR DEP. REAG.)	24
SULFUR IN SAMPLES	6
SULFUR DISSOLVED(AS SO4) IN LEACH REAGENT	36
SULFUR RECOVERED WITH ORGANIC SOLVENT	16
TOTAL SULFUR RECOVERED	83
LOSS (INPUT - RECOVERED)	2
PERCENT RECOVERY OF SULFUR	98

OVERALL LIQUIDS BALANCE	
REAGENT	7747
COAL MOISTURE	19
RINSE AND FILTER PAPER WATER	479
DISSOLVED ASH AND PYRITE	96
WASH WATER	22844
SOLVENT	8848
TOTAL LIQUIDS IN	40033
FILTRATE REAGENT	5984
SAMPLE AND FOAM REAGENT	992
DEPOSITED REAGENT	64
WASH FILTRATES	22048
ORGANIC FILTRATES	8307
AZEOTROPE AND ORGANIC FILTRATE WATER	274
LIQUIDS IN DRYER TRAPS	660
LIQUIDS ON EQUIPMENT	53
TOTAL LIQUID RECOVERED	38382
LOSS (IN - RECOVERED)	1651
PERCENT RECOVERY OF LIQUIDS	96

OVERALL IRON BALANCE	
STARTING COAL IRON	75
STARTING REAGENT IRON	231
TOTAL IRON INPUT	306
PROCESS COAL IRON	55
SAMPLE COAL IRON	7
REAGENT FILTRATE IRON	152
SAMPLE FILTRATE IRON	29
FOAM MATERIALS IRON	0
REACTOR WASH IRON	0
WASH FILTRATE IRON	36
TOTAL IRON RECOVERED	279
LOSS (INPUT - RECOVERED)	27
PERCENT RECOVERY OF IRON	91

Reproduced from
best available copy.

The "liquids balance" entries do not require explanation; they represent direct or by difference weight measurements. The entry "sample and foam reagent" could be an exception. In the majority of experiments, the weight of liquid shown for this entry represents the quantity of reagent drawn during reactor slurry sampling. In early experimentation, however, we experienced some slurry foaming during the early stages of L-R processing; as a result a small quantity of foam left the reactor through the oxygen exhaust valve. This foam was trapped, weighed, filtered, and analyzed. Its components (principally reagent) were then entered in the appropriate mass balances. It should also be noted that the "dissolved pyrite and ash" entry in the "liquids balance" does not include the produced elemental sulfur; the latter is part of the "organic filtrate" entry.

In the "overall coal sulfur balance" the "input", "process coal", and "sample" sulfur values were determined from coal weights and Eschka analyses. The processed coal and samples sulfur values were corrected for deposited reagent sulfate. The "sulfur recovered with organic solvent" was determined from sulfur analysis of the organic solvent residue. The "sulfur dissolved as sulfate" was computed from the measured pyritic sulfur removal (coal S_p analyses) by assuming that 60 percent of the removed S_p was dissolved as sulfate. This assumption was based on extensive experimentation performed on Lower Kittanning coal in the previous bench-scale program[1] which indicated that pyrite removed from coal by the Meyers Process was converted and recovered as sulfate sulfur and elemental sulfur at a ratio estimated to be 1.5 (the ratio was estimated from coal S_p analyses and ferrous ion production). Within experimental uncertainty, the same ratio appears valid for this program's coal, even when processed under L-R conditions at as high a temperature as 130°C. In the majority of experiments, the recovered elemental sulfur equalled 32-35 percent of the S_p removed from the coal instead of the expected 40 percent; this computes to S_s/S_n ratios in the range of 1.8 to 2.1 (Experiment 1 represents an exception in that the recovered S_n is less than 30 percent of the estimated removed S_p). However, complete elemental sulfur recovery is difficult and the determination of recovered elemental sulfur is subject to error. During the previous program, elemental sulfur recovery based on an S_s/S_n ratio of 1.5 range between 80-90 percent (32-36 percent of the removed pyritic sulfur).

The same appears to be true with the present coal based on the quantity of elemental sulfur recovered and the S_p removals as computed from coal analyses before and after processing. (In the previous program the S_s/S_n ratios were also verified from Fe^{+2} production; because of Fe^{+2} oxidation during L-R operation this verification technique could not be used in the majority of experiments performed in the current program.)

It should be noted that 80-90 percent elemental sulfur recovery does not necessarily imply that this sulfur product was incompletely removed from coal. Incomplete recovery from toluene (the extraction medium), small errors in analysis or weighing of the sulfur residue, and small errors in the computation of S_p removal can easily account for 10-20 percent elemental sulfur deficiency.

The "iron balance" entries were computed from weight measurements and iron analyses. The origin of each entry is evident from its label.

2.4 DATA DISCUSSION AND INTERPRETATION

The data in Appendices A through C (Volume 2) indicate that in the majority of the L-R experiments performed the overall process mass balance of solids, liquids, sulfur, and iron were better than ± 5 percent; individual unit operation mass balances were even better. In view of the fact that the overall process mass balances of each experiment involved over one hundred weight measurements and analysis determinations, that each experiment involved several manual slurry transfers, and that the system was relatively small (e.g., the sulfur balance involves less than 100 grams of sulfur in most cases), the mass balances attained should be considered excellent. In the rare cases where larger than 5 percent discrepancies occurred in one or more of the "balanced" quantities, the discrepancy was probably due to untraceable errors in weights and analyses rather than losses during processing. The biggest losses were in liquids and they represent water evaporation losses during coal washing. In general, the mass balance results indicate that the data can be used with confidence in drawing conclusions on the effectiveness of L-R processing on the leaching of pyrite from Lower Kittanning coal. Individual pieces of data or data involving a small portion of the processed slurry could, of course, be in substantial error and yet not influence the described mass balances. In fact, this was the case with a number of reactor samples, as indicated in the previous section.

The raw rate data in the same Appendices of this report (Volume 2) do not exhibit the consistency of the mass balance data. However, these apparent inconsistencies are explainable. It will be shown later that, despite some scatter, the data are internally consistent and relatable to that generated under ambient pressure processing in the previous bench-scale program (separate leaching-regeneration operations).

The scatter in rate data was traced to three causes: sampling (especially reactor slurry sampling), sulfur forms analyses, and oxygen deficiency. The problems experienced in sampling and sulfur forms analyses were alluded to earlier. In general, slurry sampling improved greatly when "dead spots" were eliminated from the reactor sampling loop and when slurry foaming was reduced substantially by "wetting" the coal in the mixer section. The only consistently poor sample was the one taken at the start of L-R operation, most likely because coal particle size distribution homogeneity had not yet been accomplished in the reactor (this sample was taken almost immediately after the start of slurry circulation). However, the S_p content of coal at the start of L-R was determined from the quantity of ferrous ion produced during t_m and a poor coal sample at the start of L-R did not present problems in data interpretation. The inconsistencies in sulfur forms analyses were substantially reduced through the application of the organic sulfur correction to S_p discussed in the previous section (Equation (2), page 28). Oxygen deficiency during L-R processing was probably the single most important reason for the observed rate data scatter and it was certainly the one responsible for the larger deviations in the L-R rate data. (Oxygen was used during L-R processing to regenerate the Fe^{+3} being depleted by pyrite oxidation. Oxygen concentration influences the Fe^{+2} to Fe^{+3} conversion rate; the iron forms the pyrite oxidation rate as explained below.)

According to data derived from ambient pressure processing of Lower Kittanning by the Meyers Process each mole of pyrite leached from coal consumes (reduces) 9.2 moles of Fe^{+3} and produces 10.2 moles of Fe^{+2}. The quantity of elemental sulfur produced during L-R processing appears to indicate that the same stoichiometry applies to this mode of processing. Ambient pressure data also indicated that the S_p leaching rate depends on the square of the Fe^{+3}-to-Fe ratio, Y. If the same rate dependence on Y exists under L-R processing, a small change in the Y value should translate into substantial effect on the S_p removal rate. This appears to be the case upon analysis of the "rate data" Tables contained in Appendices A and B, Volume 2. Since oxygen is used to regenerate Fe^{+3} (one mole of oxygen regenerates four moles of Fe^{+3}), even a small deficiency in oxygen during L-R processing can have a pronounced effect on S_p leaching rate through its influence on Y.

The above discussion is illustrated by the data depicted in Figure 3. This figure summarizes the data from 14 experiments performed on 14 mesh top size coal under the conditions indicated (data from Tables B-1, B-2, B-3 and B-4, Appendix B, (Volume 2). The remaining data on this size coal (110°C and 130°C, Tables B-5 and B-6) were not included in order to avoid additional clutter of the plotted data; however, it can be easily established through inspection of Tables 5 and 6 that the majority of these data fall within the band traced by the plotted data. In order to minimize data scatter from errors in sulfur forms analyses the "corrected" S_p removals during t_m were estimated from ferrous ion production; all other data was derived from direct coal analyses of reactor samples and product coal samples. The data designated by bars (samples from 4 experiments) and that labeled as "outlier samples" were derived from experiments processed under identical conditions except for small differences in the starting reagent Y. The plotted data indicate that during L-R processing the only discernible parametric effect is that of slurry concentration during the first hour of processing which could be reasoned to be just an apparent effect due to the higher S_p removal during t_m. In fact, the "outlier samples" deviate more from the mean of the plotted data than any sample representing parameteric variations. These outliers represent samples from Experiments 30 and 31 (Table B-2). The Y values of these samples differ only by approximately

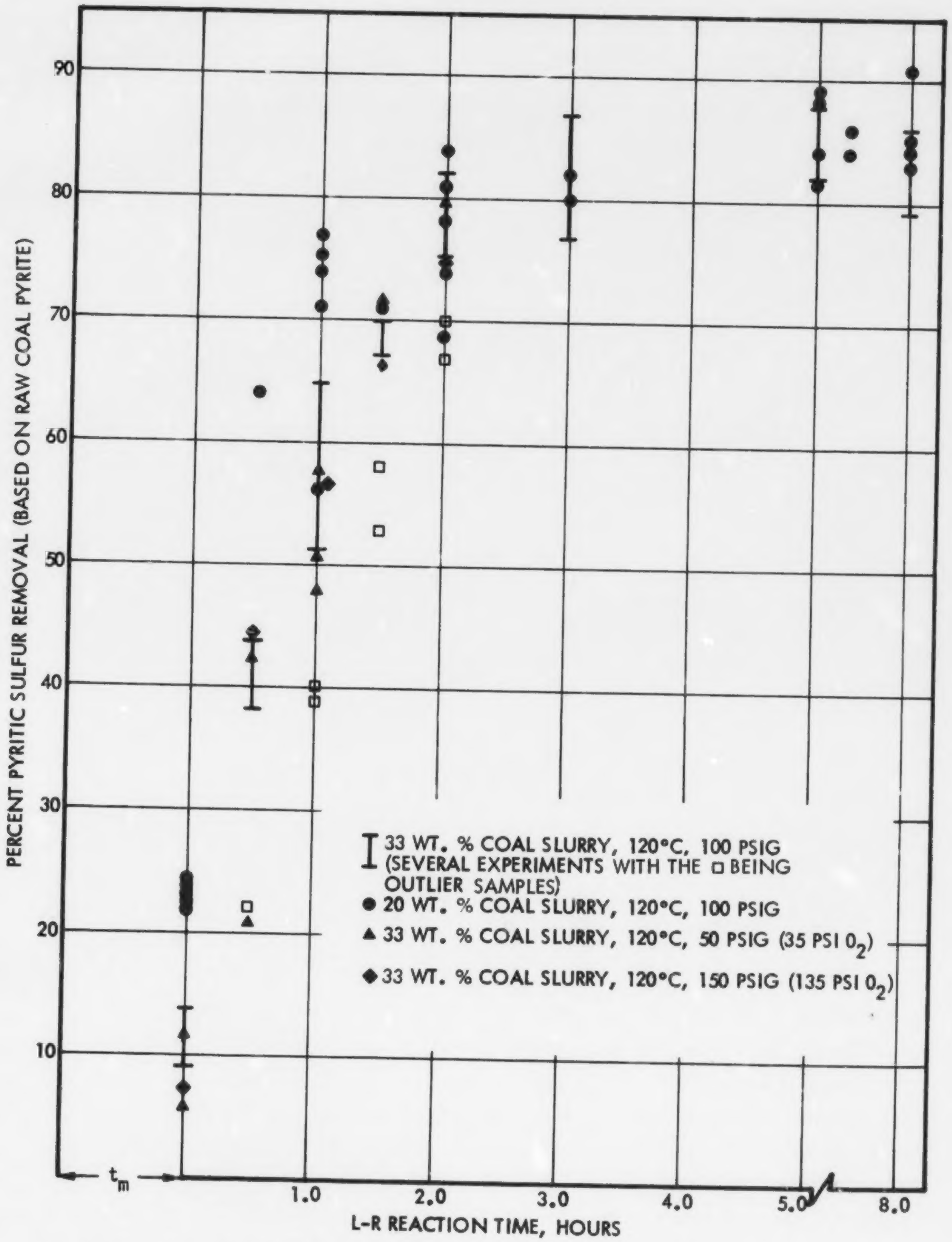


Figure 3. Pyritic Sulfur Removal from 14 Mesh Top Size L.K. Coal Processed at 120°C with 5 Wt. % Fe Reagent (Data Summary)

0.10 from those of corresponding data from Experiment 28 (or from the average Y of all the experiments represented by the bars in Figure 3); however, the indicated S_p removals differ by nearly 100 percent at t_{L-R} = 0.5 hours (22 percent versus 42 percent for the average of the "bar" data) and nearly 50 percent at t_{L-R} = 1.0 hour (39 or 40 percent versus 58 percent for the averaged data). This example does not only illustrate the difficulty of sensing oxygen deficiency during L-R processing, but it also underscores the importance of Y to pyrite leaching rates and it appears to indicate that ferric ion is the oxidizing agent in pyrite removal during L-R processing just as it was determined to be during ambient pressure processing (separate leaching-regeneration). It can be concluded, therefore, that under efficient regeneration the S_p removal rates during L-R should be at least as high as those indicated by the upper bounds of the plotted data. This translates to 80-85 percent pyritic sulfur removal from 14 mesh x 0 Lower Kittanning coal after approximately two hours of L-R processing plus t_m. Since results from the previous bench-scale program indicated that the same extent of S_p removal required 10-12 hours of ambient pressure processing at 102°C the L-R S_p removal rate at the 110°-130°C range must be substantially higher than that obtained at 102°C with separate regeneration. This conclusion is fully validated in Section 2.4.2.

Oxygen deficiency during part of the experimentation could have been the result of insufficient feed rate or inadequate mixing due to deficient apparatus design or inappropriate procedures; or it could have been unavoidable because the demand of oxygen by the system exceeded theoretical limitations (e.g., maximum oxygen solubility in the slurry) or practical means of oxygen incorporation into the slurry. The scatter in the data of nearly identically processed coal tends to indicate that the oxygen deficiency was due to inadequate experimentation rather than being due to unavoidable causes. Thus, it is our opinion that conclusions concerning the efficiency of L-R processing should be based on the assumption of efficient regeneration (rate of Fe^{+3} regeneration as predicted by the kinetics of the reaction).

The scatter in the data, the apparent insensitivity to parametric changes, and the nearly abrupt reduction in S_p removal rate after two hours of L-R processing (Figure 3) hindered initial efforts to apply previously derived rate expressions on leaching and on regeneration to L-R processing or to develop new ones which adequately described the process. It was not until virtually the complete set of data was generated that the oxygen deficiency probability became apparent and that the flattening of the S_p removal rate became statistically valid. Once these unexpected occurrences were recognized, it became evident that a single rate expression (or at least a single rate constant expression) can not describe the entire leaching operation of this particular coal and that Y values predicted from the simultaneous solution of previously derived S_p leaching rate and Fe^{+3} regeneration rate expressions would not predict the generated data. The coal leaching process, therefore, was divided into four parts (processing ranges) and the data derived from each one were examined separately. The four processing ranges are: (a) mixer processing, (b) L-R processing up to 80 percent S_p removal, (c) L-R processing between 80-90 percent S_p removal (2-8 hours L-R processing), and (d) "settler" processing. Data discussion and process definition in the outlined four processing ranges are presented in the ensuing report sections in which process behavior in each major process unit operation is described and discussed separately.

The above discussion and conclusions apply to the L-R processing of 100 mesh top size coal as well (data in Appendix A, Volume 2).

2.4.1 Mixer Unit Operation

Initially, the "Mixer Unit Operation" was defined as that part of processing where hot, approximately 70°C, reagent was mixed with "as received" coal and the resulting slurry, pressurized by nitrogen gas to the desired L-R pressure, was heated to the desired L-R temperature. However, substantial slurry foaming during L-R processing, especially in the early stages of L-R processing, required that the mixer section be modified so as to furnish a substantially non-foaming slurry to the L-R section.

An extensive small scale investigation (200-500 grams of coal) was undertaken in order to identify the causes of coal slurry foaming, to establish practical foam control methods, and to define the proper "mixer section" for L-R processing of suspendable coal. The following parameters were examined for their effect on coal slurry foaming and its control: slurry pH, iron salt concentration and Y of reagent, slurry solids content, coal particle size, coal moisture, slurry temperature, retention time near slurry boiling temperatures, anti-foam agents, wetting agents, coal washing (soaking in hot water), and slurry reflux. In addition, the foaming characteristics of processed and raw coal slurries were compared and the gas evolved (principally CO_2) from raw coal treated with acids was determined. The quantity of foam (height in a reactor column) generated during boiling of the coal slurry after treatment, or after additives had been incorporated, and its consistency (solids content and persistence) served as criteria for measuring the various effects.

Slurry pH (in the range of 1 to 7), the Y of reagent, slurry temperature up to boiling and "soaking" time up to 2 hours at any temperature in this range, anti-foam agents, and coal washing did not affect slurry foaming. Slurry foaming decreased with decreasing iron concentration, but it remained at unacceptable levels even when iron was reduced to zero (dilute sulfuric acid or water coal slurries). Foam volume, density, and stability increased with increasing solids content in the slurry; however, even very dilute slurries foamed. The maximum CO_2 evolution measured (approximately 150cc of gas per kilogram of coal) was not sufficient to account for the volume of the generated foam. Slurry foaming increased with decreasing coal top size in the range of 14 to 200 mesh, but it remained at unacceptable levels even with the 14 mesh x 0 coal; removal of the 200 x 0 fraction from the 14 mesh top size coal reduced slurry foaming substantially and rendered the 14 x 200 mesh coal processable. Wetting agents changed the nature (consistency) of the foam radically, but not its volume; the normally thick, black slurry foam was converted to thin (soap like), clean foam. Combinations of wetting and anti-foam agents arrested slurry foaming completely. Slurry reflux at ambient pressure for approximately 30 minutes virtually eliminated slurry foaming. Finally, the moisture content of coal appeared to have an effect on the volume and density of coal slurry foaming with slurry foaming decreasing with increasing coal moisture content, i.e., the coal was in essence "pre-wetted".

The above investigations led to the conclusion that the principal cause of slurry foaming is the presence of dry (unwetted) coal in the slurry and that Lower Kittanning coal which equilibrates in air to only about one percent moisture is difficult to wet. Three approaches rendered Lower Kittanning coal slurries processable through L-R: (a) coal wetting through the addition of wetting and anti-foam agents, (b) slurry reflux for approximately 30 minutes and (c) removal of coal fines (200 mesh x 0 fraction) prior to processing. All three methods were tested in bench-scale L-R processing runs and all proved successful. However, removal of the fines fraction (a substantial portion of suspendable coal) was the least desirable method because a different technique had to be identified for processing the fines by the Meyers Process and because this approach was not as effective in foam control as coal wetting. The wetting, anti-foam agent approach was rejected because of the cost of these agents and because it appeared to adversely affect L-R processing (refer to data in Tables A-7 and B-7, Volume 2); this method would have been used if foam arrest by slurry reflux did not prove successful. The slurry reflux method was judged to be by far the most desirable because of its simplicity and easy adaption to L-R processing. This approach was therefore, selected for incorporation into the "mixer unit operation" as standard practice.

Mixer processing, "mixer unit operation", in all suspendable coal experiments involving simultaneous leaching-regeneration (except for the two experiments in which wetting agents were used) consisted of the following steps: slurry preparation and heating to reflux temperature (102°C) slurry defoaming by 30 minutes reflux, slurry transfer to the L-R reactor and pressurization, and slurry heating to the desired L-R temperature. Normal slurry mixer processing times, t_m, ranged between 1.0 and 1.5 hours; occasionally, longer times were used either because foaming persisted or because of equipment problems. The approximately 10 kilograms of slurry used in each experiment was prepared with 65° to 70°C reagent, split into 3-4 four-liter glass flasks equipped with condensers, and transferred to the 13-liter stainless steel L-R reactor when defoaming was completed. The temperature-pressure-time history of mixer processing was recorded in detail during each experiment. Figure 4 depicts typical mixer processing conditions.

Pyritic sulfur removal from coal during t_m varied from near zero (less than 5%) in experiments where no-iron containing starting reagent was used to nearly 30 percent when coal was processed with 5 wt. percent iron reagent as 20 weight percent slurry for longer than normal t_m. Shorter t_m, 3 weight percent Fe reagent, and 33 percent coal slurries gave intermediate S_p removals (see data in Appendices A, B, and C, Volume 2). This type of parametric behavior was expected from previous experience with ambient pressure processing of Lower Kittanning coals. The next step was to investigate the predictability of the t_m data generated in this program by the pyritic sulfur leaching rate expression developed in the previous bench-scale program (EPA contract EHSD 71-7) from ambient pressure data generated at 70°, 85°, and 102°C on a similar Lower Kittanning coal, namely,

$$r_L = - \frac{dWp}{dt} = K_L W_p^2 Y^2, \qquad (3)$$

where

r_L	is the pyrite leaching rate, expressed in weight of pyrite removed per 100 weights of coal per hour (rate of coal pyrite conc. reduction),
W_p	is the pyrite concentration in coal at time t in wt. percent,
t	is the reaction (leaching) time in hours,
Y	is the ferric ion-to-total iron ratio in the leacher at time t, dimensionless, and
K_L	is the pyrite leaching rate constant (a function of temperature and coal particle size) expressed in $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$

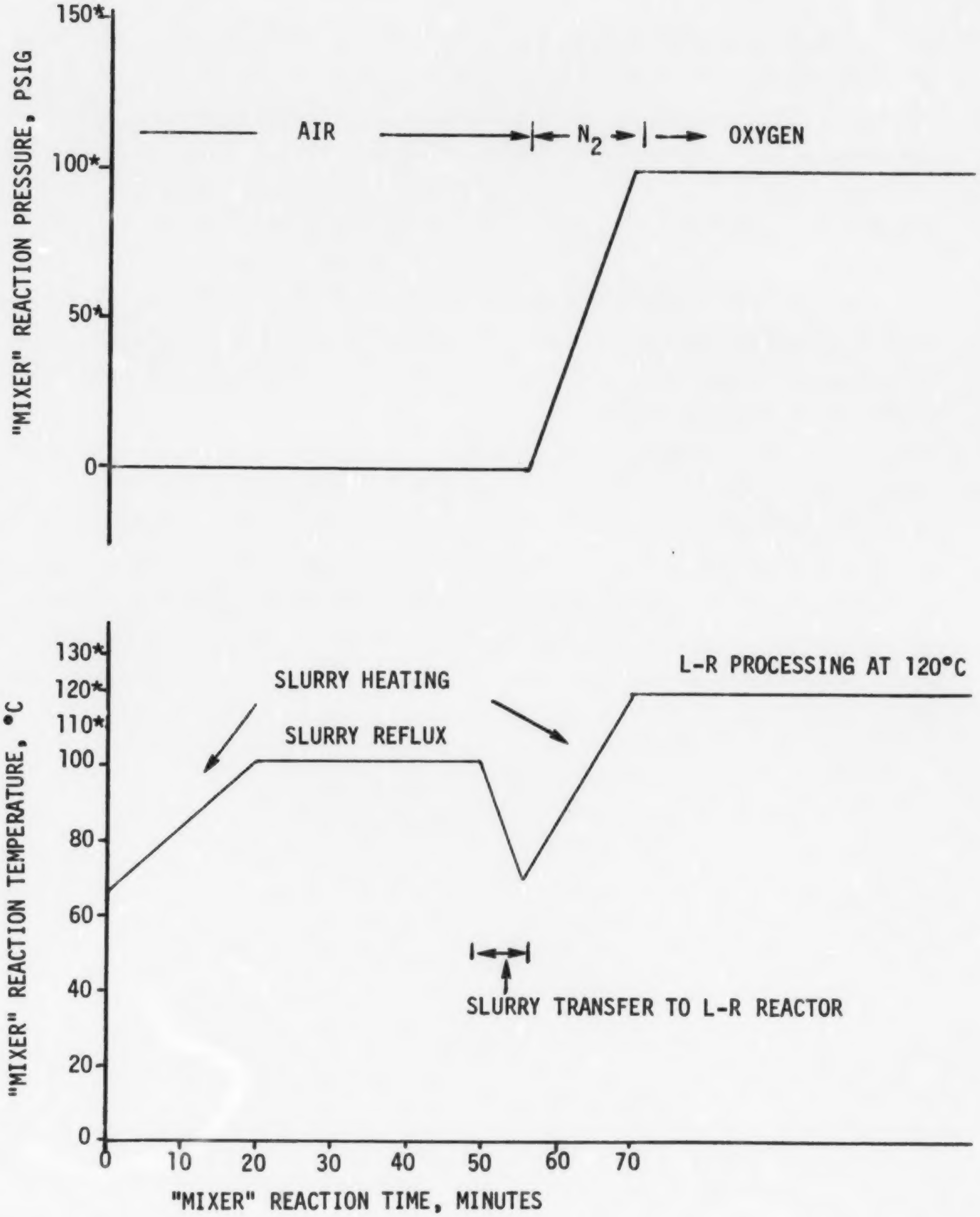


Figure 4. Typical Mixer Processing Conditions

with

---

*Utilized L-R Temperatures and Pressures

$$K_L = A_L \exp(-E_L/RT), \qquad (4)$$

where

A_L is the Arrhenius frequency factor in the units of K_L,

E_L is the apparent activation energy in calories/mole,

R is the gas constant in calories/mole°K, and

T is the absolute temperature, in °K

From data generated in the previous bench-scale program, the K_L value for pyrite leaching from 100 mesh x 0 L.K. coal at 102°C was determined to be between 0.12 and 0.15 $(\text{hours})^{-1}$ $(\text{wt. percent pyrite})^{-1}$. The corresponding K_L values for 85°C and 70°C leaching were 0.09 and 0.03, respectively. The Arrhenius plot of these three rate constants did not furnish the expected straight line; thus, the A_L and E_L values derived from these constants and reported in Reference 1 were based on the 85°C and 102°C data. Recent review of the 85°C and 70°C data revealed that the determined rate constant for the 85°C run was 0.088 ± 0.044 while that of the 70°C data was 0.03 ± 0.013 (single experiment data for each temperature with 50 rate data points taken in each experiment). It was, therefore, concluded that the 70°C rather than the 85°C K_L value should have been used for the A_L and E_L determinations. It was also noted that a K_L value of 0.07 for the 85°C run gives a straight line Arrhenius plot for all three temperatures with K_L (102°C) = 0.15. The new data assessment led to two sets of A_L and E_L values depending on which end of the 102°C K_L range was used with the 70°C K_L value:

For 102°C $K_L = 0.15$

$A_L = 4.7 \times 10^5$ $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$ and

$E_L = 12.8$ Kcal/mole

For 102°C $K_L = 0.12$

$A_L = 3.4 \times 10^5$ $(\text{hours})^{-1}$ $(\text{wt. percent pyrite in coal})^{-1}$

$E_L = 11.1$ Kcal/mole

Similar but less extensive rate data generated with 14 mesh x 0 Lower Kittanning coal revealed that the K_L value for this size coal was approximately 20 percent lower than the corresponding K_L for 100 mesh x 0 coal; thus, at 102°C

$$0.10 \leq K_L^{14} \leq 0.12 \text{ (hours)}^{-1} \text{ (wt. percent pyrite in coal)}^{-1};$$

the corresponding A_L is

$$2.7 \times 10^5 \leq A_L^{14} \leq 3.8 \times 10^6 \qquad \text{(same units)}$$

assuming that the activation energy is the same for both top size coals, namely

$$11.1 \leq E_L \leq 12.8 \text{ Kcal/mole}$$

Prior to utilizing the above rate expressions to predict "mixer" processing, it was considered necessary that at least one ambient pressure leaching experiment be performed under continuous reagent exchange conditions with the L.K. coal used in the current program in order to compare identically generated data from the two coals (present and previous program L.K. coals). The experiment was performed at 102°C (slurry reflux temperature) with 100 mesh x 0 coal slurried in ferric sulfate solution containing 4.9 weight percent iron. The total reaction time was 8.5 hours (8.0 at 102°C plus 34 minutes slurry heating time between 70°C and 102°C). The generated rate data and overall process mass balance data are summarized in Table 7.

The first part of Table 7 (first page) shows the measured Fe^{+2}/Fe ratio (1-Y) and the computed change in coal weight, pyrite removed, average rate of removal (from reaction start to the indicated reaction time), and coal composition as a function of reaction time. The pyrite removal was computed from measured ferrous ion production as a function of time assuming that pyritic sulfur was oxidized to sulfate sulfur and elemental sulfur at the ratio of 1.5. All other computed quantities were derived from the calculated pyrite removal plus a small correction for any non-pyritic ash dissolved or added to the coal during reaction. (The

TABLE 7. PYRITE REMOVAL FROM COAL WITH IRON SULFATE SOLUTION AT 102°C AND AMBIENT PRESSURE

SUMMARY OF REACTION DATA FOR SO4/S= 1.500   LOWER KITTANNING - 100 MESH

					CALCULATED COAL ANALYSES STEP-BY-STEP					
MIN FROM START	FE+2/FE WT. RATIO	COAL WT. FREE OF S(ELEM)*	PYRITE REMOVED PCT OF INIT	CUMULATIVE RATE PCT/HR	TOTAL S WT-PCT	PYR. S WT-PCT	ORG. S WT-PCT	SO4 S WT-PCT	ASH WT-PCT	HT CONTENT BTU/LB
34	.3333	641.27	18.78	33.13	3.791	3.306	.414	.081	29.388	10637
49	.3559	634.05	23.95	29.33	3.591	3.104	.415	.081	29.323	10655
64	.3626	628.44	27.76	26.02	3.442	2.955	.416	.081	29.276	10668
79	.3294	622.65	32.05	24.35	3.274	2.785	.417	.081	29.221	10683
94	.2791	618.37	31.90	20.36	3.280	2.792	.417	.081	29.223	10682
109	.2682	612.95	35.03	19.28	3.157	2.668	.418	.082	29.184	10693
124	.2752	607.14	39.43	19.08	2.984	2.493	.419	.082	29.128	10709
139	.2865	601.37	43.63	18.83	2.817	2.326	.420	.082	29.074	10723
154	.2888	595.93	47.01	18.32	2.683	2.190	.421	.082	29.031	10735
169	.2813	590.81	49.89	17.68	2.571	2.078	.421	.082	28.995	10745
184	.2662	585.37	52.34	17.07	2.469	1.976	.422	.082	28.962	10754
199	.2472	580.35	54.05	16.30	2.401	1.907	.422	.082	28.940	10760
214	.2373	575.03	57.19	16.03	2.275	1.780	.423	.083	28.899	10772
229	.2192	570.43	58.87	15.42	2.207	1.711	.423	.083	28.877	10778
244	.2085	565.79	60.69	14.92	2.133	1.637	.424	.083	28.853	10784
259	.2050	560.92	63.17	14.63	2.032	1.536	.424	.083	28.821	10793
274	.1988	555.94	65.29	14.30	1.945	1.449	.425	.083	28.793	10801
289	.1839	551.23	66.45	13.80	1.899	1.402	.425	.083	28.778	10805
304	.1868	546.18	68.73	13.57	1.806	1.308	.426	.083	28.748	10813
319	.1825	541.32	70.41	13.24	1.738	1.239	.426	.083	28.726	10819
334	.1705	536.64	71.54	12.85	1.691	1.192	.426	.083	28.711	10823
349	.1544	532.18	72.01	12.38	1.672	1.173	.426	.083	28.705	10825
364	.1429	527.70	72.66	11.98	1.645	1.146	.426	.083	28.696	10827
379	.1329	523.26	73.76	11.68	1.600	1.100	.427	.083	28.682	10831
394	.1250	518.60	75.11	11.44	1.545	1.045	.427	.083	28.664	10836
409	.1265	513.81	76.90	11.28	1.471	.971	.427	.083	28.640	10843
424	.1245	509.14	78.38	11.09	1.410	.909	.428	.083	28.620	10848
439	.1219	504.60	79.45	10.86	1.366	.865	.428	.084	28.606	10852
454	.1154	500.08	80.23	10.60	1.334	.832	.428	.084	28.596	10855
469	.1123	495.53	81.15	10.38	1.296	.794	.428	.084	28.583	10859
484	.1103	490.95	82.13	10.18	1.255	.753	.429	.084	28.570	10862
499	.0946	486.83	81.93	9.85	1.263	.761	.429	.084	28.573	10861
514	.0771	482.88	81.24	9.48	1.292	.790	.429	.084	28.582	10859
FROM FINAL COAL ANALYSIS			83.64		1.670	.690	.750	.230	28.550	11013

---

[*] Coal weight in grams

TABLE 7. (CONTINUED)

LOWER KITTANNING - 100 MESH
OVERALL PROCESS BALANCES FOR SOLIDS, LIQUIDS, SULFUR AND IRON*

SOLIDS BALANCE	
DRY COAL INPUT	653.0
SOLIDS REMOVED IN SAMPLES AND FILTERS	149.4
ASH AND PYRITE DISSOLVED DURING REACTION	18.3
SULFUR AND COAL IN SOLVENT EXTRACT	7.2
RECOVERED FROM FILTER PAPERS	3.0
FINAL OVEN DRIED COAL RECOVERED	470.0
TOTAL SOLIDS RECOVERED	647.9
BALANCE (RECOVERED-INPUT)	-5.1
PERCENT RECOVERY OF SOLIDS	99.2

LIQUIDS BALANCE	
LEACH REAGENT INPUT	18893.0
ASH AND PYRITE DISSOLVED DURING REACTION	18.3
TOTAL WATER (WASHES AND WETTING FILTERS)	4328.0
TOTAL ORGANIC SOLVENT INPUT	1818.0
TOTAL LIQUIDS IN	25057.3
LEACH REAGENT RECOVERED	17723.0
LIQUID REMOVED IN SAMPLES AND FILTERS	580.8
TOTAL WASH FILTRATES	4306.0
SOLVENT DISTILLATE	1742.0
LIQUIDS IN DRIER TRAPS	120.0
FOUND ON EQUIPMENT AND FINAL FILTER PAPERS	3.0
TOTAL LIQUIDS RECOVERED	24574.8
BALANCE (RECOVERED-INPUT)	-482.6
COMPUTED EVAPORATION LOSSES FROM FILTERS	0.0
ESTIMATED OVERALL BALANCE	-482.6
PERCENT RECOVERY OF LIQUIDS	98.1

COAL SULFUR BALANCE	
SULFUR IN COAL INPUT	29.5
SULFUR IN PROCESSED COAL	7.9
SULFUR IN SAMPLES TAKEN DURING REACTION	5.3
SULFUR DISSOLVED (AS SO4) IN LEACH REAGENT	11.5
SULFUR RECOVERED FROM ORGANIC SOLVENT	7.0
BALANCE (RECOVERED-INPUT)	2.2
PERCENT RECOVERY OF SULFUR	107.4

IRON BALANCE	
IRON IN COAL	24.7
IRON IN LEACH REAGENT INPUT	927.6
TOTAL IRON INPUT	952.4
IRON IN LEACH REAGENT DRAWN FROM REACTOR	734.9
IRON IN SAMPLES DRAWN DURING REACTION	37.7
IRON IN INTERMEDIATE FILTRATES REMOVED	0.0
IRON IN FINAL FILTRATE AND WASHES	179.9
IRON IN PROCESSED COAL	7.3
TOTAL IRON RECOVERED	959.9
BALANCE (RECOVERED-INPUT)	7.5
PERCENT RECOVERY OF IRON	100.8

---

*Weights are in grams

Reproduced from best available copy.

correction is made by linearly adding to or subtracting from the coal being processed any ash in excess or in deficiency from that calculated by subtracting the pyritic ash removed from the ash in the starting coal; the quantity to be added or subtracted is determined from ash analyses of the starting and processed coals.) The last line in the table shows the processed coal composition data obtained from direct coal analyses and the percent pyrite removal based on pyrite analyses of starting and processed coal.

The data in Table 7 show that the agreement in pyrite removal values determined from ferrous ion production and from direct coal analyses was very good. The discrepancy in the corresponding total sulfur content values is believed to be due to reagent iron sulfate left on the coal because of insufficient washing. The higher than expected ash content of the processed coal and the 2.2 grams of excess recovered sulfur (see "sulfur balance" on second page of Table 7) supports the above assumption and indicates that the abnormally high organic sulfur value of the analyzed processed coal must be due at least in part to unwashed sulfate. The obtained process mass balance was, also, very good, especially if our assumption concerning sulfate deposition is valid. Based on recovered elemental sulfur, the $S_s/S_n = 1.7$; or, conversely, if the true S_s/S_n is 1.5, 90 percent of the product elemental sulfur was recovered. Thus, in every aspect the data was similar to that generated with the lower ash Lower Kittanning coal used in the previous bench-scale program. In fact, the data in Table 7 is nearly identical point-by-point with that generated from Experiment 50 of the previous program.

The rate data from Table 7 were utilized in Equation (3) to determine the value of K_L at 102°C for this coal. The computed K_L was equal to 0.12 $(\text{hours})^{-1}$ $(W_p)^{-1}$ which corresponds with the lower end of the K_L range determined in the previous program. It was, therefore, decided to use the following A_L and E_L values in Expression (4) to predict coal processing in the mixer:

100 mesh x 0 coal: $A_L = 3.4 \times 10^5$ (hours)$^{-1}$ $(W_p)^{-1}$

14 mesh x 0 coal : $A_L = 2.7 \times 10^5$ (hours)$^{-1}$ $(W_p)^{-1}$

Both top sizes : $E_L = 11.1$ kilocalories per mole

Table 8 summarizes experimentally derived and predicted data for "mixer" processing of 100 mesh and 14 mesh top size Lower Kittanning coal. The data from 15 experiments of each top size coal are presented. The agreement between calculated Y, W_p, and extent of pyrite removal values at t_m and those predicted by Expressions 3 and 4 is very good; the rare exceptions are apparently due to errors in iron-forms analyses. It should be noted that the experiments in Table 8 were performed with a number of different starting slurry and reagent compositions (see data in Appendices A and B, Volume 2) and for differing reaction times, t_m, and temperature-time history. The data in Table 8 justify the use of Expressions (3) and (4) and the quoted values of A_L and E_L for the design of the "mixer" for processing Lower Kittanning coals up to 14 mesh top size.

A complete set of mixer processing data for all experiments in Appendices A and B is included in Appendix D, Volume 2 together with predicted data on L-R processing.

2.4.2 L-R Unit Operation

The L-R unit operation combines the two major Meyers Process operations, coal pyrite leaching and reagent regeneration, into a single unit. Its experimental investigation constituted the major thrust of this program.

L-R processing (simultaneous coal leaching-reagent regeneration) starts when oxygen is introduced to the slurry at the conclusion of mixer processing. During this program, L-R processing was performed at constant temperature and pressure; however, three values of each of these parameters

TABLE 8. MEASURED AND PREDICTED PYRITE REMOVAL AT THE "MIXER UNIT OPERATION"

Exp. No.	Starting		Measured and Predicted Values at $t = t_m$					
			Y		W_p		% S_p Removal	
	Y	W_p	Meas.	Pred.*	Meas.**	Pred.*	Meas.**	Pred.*
A. 100 Mesh Top Size Coal								
1	1.0	7.55	0.28	0.27	5.79	5.65	25	27
2	1.0	7.55	0.34	0.38	6.08	5.95	21	23
3	1.0	7.55	0.40	0.31	5.76	5.69	25	26
4	1.0	7.55	0.29	0.27	5.91	5.68	23	26
5	1.0	7.55	0.29	0.29	5.97	5.62	22	27
6	0.76	7.55	0.35	0.28	6.58	6.09	14	21
7	0.95	7.27	0.54	0.58	5.62	5.65	24	24
8	0.91	7.27	0.51	0.51	5.89	5.62	20	24
9	0.82	7.27	0.46	0.45	5.94	5.70	20	23
10	0.92	7.27	0.37	0.42	5.07	5.19	32	30
11	0.86	7.27	0.40	0.42	5.35	5.37	28	28
12	1.0	7.27	0.45	0.47	5.16	5.08	31	32
13	0.73	7.27	0.33	0.32	6.48	6.42	12	12
14	0.75	7.27	0.34	0.34	6.40	6.38	13	13
15	0.88	7.27	0.23	0.22	6.31	6.09	14	17
B. 14 Mesh Top Size Coal								
23	1.0	7.27	0.59	0.56	5.55	5.44	25	27
24	0.87	7.27	0.49	0.47	5.69	5.58	23	25
25	0.94	7.27	0.56	0.53	5.65	5.63	24	24
26	0.95	7.27	0.55	0.53	5.59	5.50	25	26
27	0.94	7.27	0.57	0.55	5.75	5.57	22	25
28	0.71	7.27	0.33	0.28	6.53	6.37	11	13
29	0.80	7.27	0.36	0.31	6.35	6.23	14	15
30	0.67	7.27	0.30	0.26	6.49	6.40	11	13
31	0.62	7.27	0.30	0.28	6.63	6.56	9	10
32	0.84	7.27	0.41	0.35	6.41	6.24	13	15
33	0.84	7.27	0.39	0.31	6.35	6.16	14	16
34	0.45	7.27	0.26	0.25	6.87	6.85	6	6
35	0.77	7.27	0.37	0.33	6.46	6.34	12	14
36	0.52	7.27	0.29	0.26	6.81	6.70	7	8
37	0.70	7.27	0.43	0.32	6.71	6.45	8	12

---

* Predicted values from $r_L = K_L W_p^{(2)} Y^{(2)}$ and $K_L = A_L \exp(-E/RT)$

** Calculated values from measured ferrous ion production were used. The majority of experimentation was performed at 120°C and 100 psig (85 psi O_2) with 100 mesh and 14 mesh top size Lower Kittanning coal. The major objective was the investigation of coal pyrite leaching efficiency under L-R processing; thus, reaction time was the parameter most thoroughly studied. The generated data has been tabulated as a function of this parameter (Appendices A through D, Volume 2). Slurry composition (solids content, reagent composition, and reagent pH) was also varied with each top size coal. The data from approximately 50 experiments were utilized to determine the efficiency of this unit operation and its sensitivity to changes in process parameters.

Pyrite leaching from coal during slurry preparation necessitated that the L-R unit operation be investigated in conjunction with the mixer operation. However, the data presented in the previous section (Section 2.4.1) demonstrated that process performance in the mixer could be accurately defined; thus, the L-R operation could be evaluated separately even though the experimentation involved both unit operations. In fact, the predictability of mixer performance by the use of Equations (3) and (4) suggested that the L-R operation performance should be also predictable through the simultaneous use of the above equations and those for reagent regeneration developed in the previous bench-scale program, namely

$$r_R = -\frac{dFe^{+2}}{dt} = K_R P_{O_2} (Fe^{+2})^2, \qquad (5)$$

where

r_R moles of ferric ion regenerated per unit time,

P_{O_2} oxygen partial pressure in atmospheres,

Fe^{+2} ferrous ion concentration in moles per liter,

K_R rate constant, a function of temperature only, in liters/mole-atm-unit time and

$$K_R = A_R \exp(-E_R/RT) \qquad (6)$$

with

$$A_R = 6.7 \times 10^5 \text{ Liters/Mole-Atm-Min}$$

and

$$E_R = 13.2 \text{ Kcal/Mole.}$$

However, attempts to predict the S_p (pyritic sulfur content of coal) versus t_{L-R} (L-R reaction time) data contained in Appendices A and B, Volume 2, through the simultaneous solution of Equations (3) through (6) failed. In general, the experimentally determined pyrite removal rates were higher than the predicted rates up to approximately 80 percent removal and lower thereafter; also, the measured Y values (Fe^{+3}-to-Fe ratio) were lower than the predicted Y values.

Comparison of the predicted and experimentally derived data led to the following observations:

- The pyrite leaching rate during L-R processing at constant temperature depended only on W_p and Y. The magnitude of the rate dependence on these variables appeared to be the same as that determined for ambient pressure leaching of Lower Kittanning coals; thus, Equation (3) should have predicted the experimental S_p versus t data in all Meyers Process unit operations if correct K_L and Y values were used.

- The K_L (leaching rate constant) values predicted through Equation (4) for L-R leaching were substantially lower than the experimental K_L values suggested by the pyrite removal data for up to nearly 80 percent removal (it was indicated earlier that the experimental rates were higher than the predicted rates even though the corresponding measured Ys were lower than the predicted). This lack of predictability of the L-R K_L from A_L and E_L values determined under ambient pressure processing of coal could be suggesting that K_L should not be treated as a single constant, but as a sum of rate constants each of which relates to a certain coal or pyrite particle size within a given coal top size; however, the generated data did not permit verification of this possibility.

- The experimental data indicated that the L-R pyrite leaching rate was dropping faster than predicted by Equation (3) with a single valued K_L (isothermal processing) when pyrite removal exceeded approximately 80 percent. This observation implied a possible change in reaction mechanism; however, the data indicated continued leaching rate dependence on W_p and Y. Again, a change in K_L value was indicated which because of the isothermal processing was not predictable by Equation (4) (in principle, this change in K_L value could have been predicted if K_L was indeed a sum of rate constants of known values).

- The low measured Ys in comparison to Ys predicted through the simultaneous solution of Equations (3) through (6) and the large variances in the deltas between measured and predicted Ys, especially during early L-R processing when pyrite leaching rate was the highest, led to the conclusion that reagent regeneration during many of the experiments was inefficient due to incomplete mixing (e.g., inappropriate Reynolds Number in the slurry circulation loop), although lack of adequate oxygen supply could not be ruled out for certain experiments involving 33 wt. percent coal slurries. Equations (5) and (6) proved repeatedly valid during separate reagent regeneration experimentation performed in the parametric ranges that L-R processing was performed. There is no reason to believe that the presence of coal could have had an inhibiting effect on regeneration rate unless it affected oxygen mixing (there was no evidence of direct reaction of oxygen with coal).

The above observations led to the following tentative conclusions concerning pyrite leaching data predictability by Equations (3) through (6):

- Pyrite removal versus leaching time data generated from suspendable L.K. coal in the Meyers Process unit operations investigated in this program (Mixer, L-R, and Settler Operations) should be predictable by Equations (3) through (6). The only input data required are: starting coal pyrite concentration, starting reagent iron and ferrous ion concentrations, the oxygen partial pressure during L-R processing, the temperature-time curve of the process, and the values of the Arrhenius constants A and E for Equations (4) and (6). If the L-R processing behavior of the coal used in this program is typical of L.K. coals, then more than one pair of A and E values will be needed for Equation (4) for each coal top size. This is tantamount to saying that Equation (3) should be most properly expressed as

$$r_L = -\frac{dW_p}{dt} = \sum K_i {W_p}^2 Y^2, \tag{7}$$

$$r_L = -\frac{dW_p}{dt} = \bar{\sum}(KW_p^2)_i Y^2 \tag{8}$$

  with each K_i depending on a different pair of A and E values. The K_i and W_{pi} values are specific either to narrow coal or pyrite particle sizes within a given top size coal or to elements of coal (shells) whose thickness is the same for all particle sizes and depends only on reagent accessibility rates (distance from coal surface and coal porosity).

- The L-R data generated in this program could not be predicted by Equations (3) through (6) because of the change in the K_L value during L-R processing and because of inconsistent regeneration during the early stages of L-R processing. However, if the conclusions reached in the previous paragraph are valid, the generated L-R data should be predictable by Equation (3) through the use of experimentally determined K_L values from L-R data and through the use of measured Y values.

In order to test the validity of the above conclusions, the L-R data in Appendices A and B, Volume 2 of this report were treated as if derived from two separate L-R operations (L-R Sections) describable by Equation (3) but with different reaction rate constants (K_L values). The first "L-R Section" involved pyrite leaching rate data up to approximately 80 percent overall pyrite removal (pyrite removal based on starting coal pyrite content); the second "L-R Section" involved the remaining L-R rate data (pyrite removal beyond 80 percent) which apparently required a lower K_L value in order to be predictable by Equation (3). A K_L value was determined for each of the two L-R Sections which was then used in conjunction with measured Y values in Equation (3) to test the predictability of the data in Appendices A and B. The K_L dependence on W_p during its transition from the high to the low value was also determined from the experimental data. The detailed procedures used and the results of the L-R rate development investigations are presented in the next section of this report.

2.4.2.1 Pyrite Leaching Rates During L-R Processing of L.K. Coal at 120°C

On the assumption that Equation (3) would prove to be the correct empirical rate expression by which pyrite removal from suspendable L.K. coal during L-R processing could be predicted, its integrated form was used to determine the K_L values applicable to 120°C L-R processing of the two top size coals (14 and 100 mesh). Equation (9) is the integrated form of Equation (3):

$$K_L = \frac{1}{t_{L-R}\bar{Y}^2} \left(\frac{1}{W_p} - \frac{1}{W_p^m}\right), \qquad (9)$$

where

K_L is the L-R rate constant for the particular coal top size applicable up to nearly 80 percent pyrite removal and expressed in $(\text{hours})^{-1}\ (W_p)^{-1}$,

t_{L-R} is the L-R reaction time in hours,

$\bar{Y}$ is the average Y value of the reagent during t_{L-R}, dimensionless quantity,

W_p is the concentration of pyrite in coal at t_{L-R}, in wt. percent,

W_p^m is the concentration of pyrite in coal at $t_{L-R} = 0$ (end of Mixer processing and start of L-R), in wt. percent.

The $\bar{Y}$ values were determined from measured Y versus t_{L-R} curves plotted from data in Appendices A and B, Volume 2. The W_p values were computed from the S_p values (pyritic sulfur concentration in coal) in Appendices A and B ($W_p = (120/64.1)\ S_p$) and the W_p^m values were obtained from Table 8, Section 2.4.1.

Over 20 data points derived from eight different experiments were used in Equation (9) in order to determine the values of K_L for each of the two top size coals and to check their constancy with changes in processing parameters other than temperature and coal particle size. These computations revealed that the most probable K_L value for L-R processing of the 100 mesh top size coal at 120°C was 0.6 $(\text{hours})^{-1}\ (W_p)^{-1}$ and the corresponding K_L value for the 14 mesh top size coal was 0.5 $(\text{hours})^{-1}\ (W_p)^{-1}$. With the exception of occasional outliers, the deviation in the K_L values was less than $\pm$ 0.1. These computations also revealed that the use of S_p values corrected for anomalies in the organic sulfur content of the coal (Equation 2, page 28) tended to minimize the deviation in the computed K_L values.

The estimated K_L values for 120°C L-R processing of 100 mesh and 14 mesh top size L.K. coals are approximately 5 times larger than K_L values determined for pyrite leaching from the corresponding coal top sizes at 102°C (Section 2.4.1). This unexpectedly high factor of five difference between the 120°C and the 102°C K_L values (Equation 4 predicts only a factor of 2 difference) was further verified from data plots similar to that illustrated in Figure 5 for 100 mesh top size coal.

In Figure 5, the top curve presents the S_p removal versus L-R reaction time data generated in Experiments 7, 8, and 9; these experiments differ only in overall L-R reaction time used (see Appendix A, Volume 2 for details on experimental conditions). The second curve presents the same type of data from Experiment 10 which because of insufficient supply of oxygen or inefficient mixing of oxygen into the slurry was performed with reagent whose Y remained low for a large part of L-R processing. It is noted that the lower Y values are reflected in lower S_p removals, as Equation (3) predicts should happen. "Corrected" S_p values were used and the present S_p removal was computed from

$$\% \ S_p \text{ Removal} = \frac{1-(S_p/S_p^m)}{1-(1.2S_p/64.1)} \times 100.^* \qquad (10)$$

The lower two curves in Figure 5 represent the expected S_p versus t (coal leaching time) data from Experiments 7 through 10 if they were performed at 102°C (ambient pressure) with Y versus S_p traces being identical at 102°C and 120°C for the corresponding experiments. These curves were generated by using a rearranged form of Equation (9), namely

$$t = \left(\frac{1}{K_L Y^2}\right)\left(\frac{64.1}{120\ S_p} - \frac{1}{W_p^m}\right) \qquad (11)$$

The required leaching time, t, was computed for attaining each of the S_p values indicated in the top two curves; curve rather than actual S_p values were used which is equivalent to using averaged data.

---

[*] Equation (10) is a more exact form of Equation 1 (page 28) because it accounts for the reduction in coal weight during reaction (pyrite dissolution); its derivation, based on pyrite mass balance, is given in Appendix E, Volume 2.

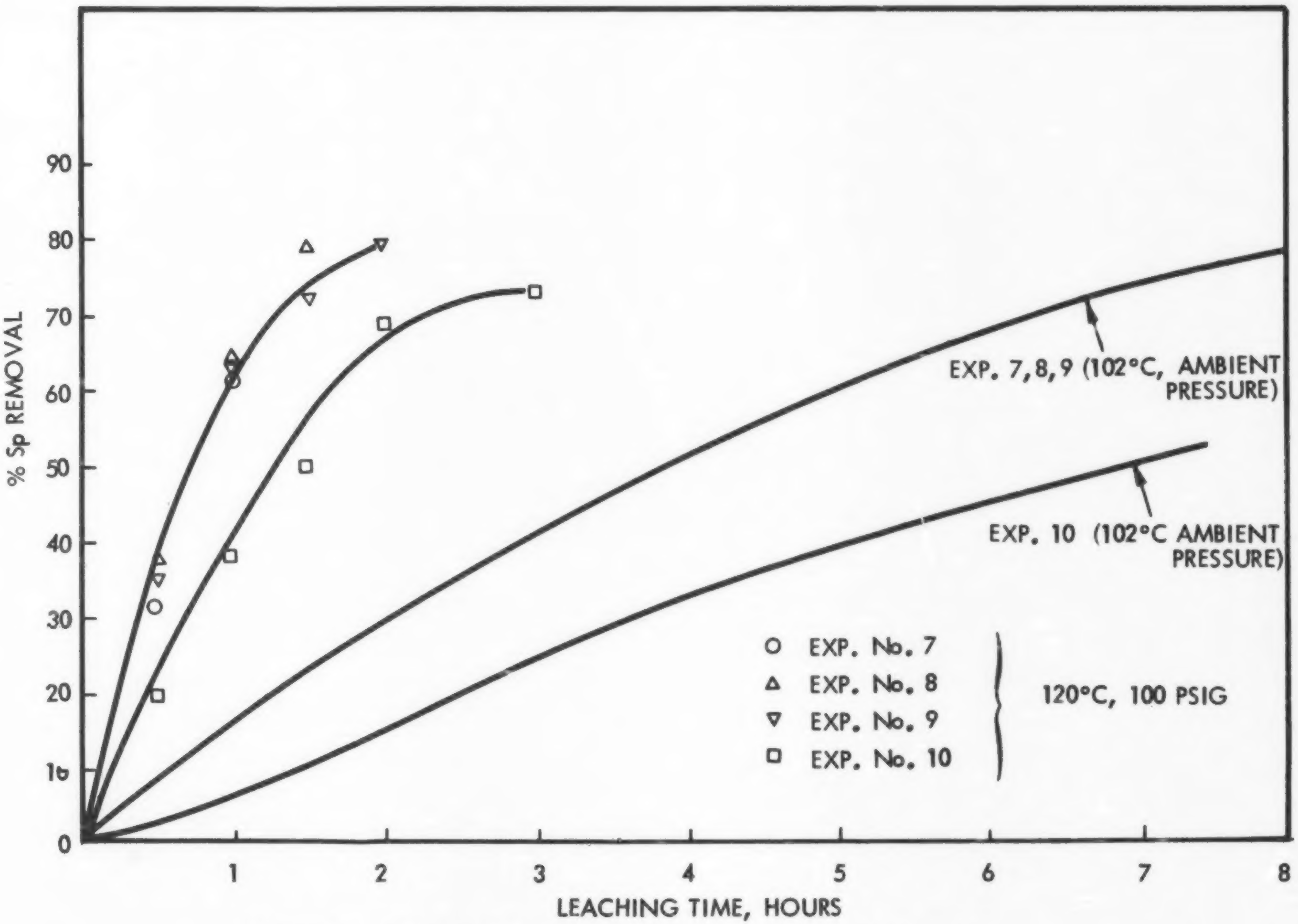


Figure 5. 100 Mesh Top Size Lower Kittanning Coal Leached with 5 Wt.% Fe Reagent (20% Slurries)

The $\bar{Y}$ values were computed as previously explained from the measured reagent Y values during the performance of Experiments 7 through 10 at 120°C; a $\bar{Y}$ was computed for each level of S_p removal. The K_L value used was that determined in Section 2.4.1 for 102°C pyrite leaching from 100 mesh top size L.K. coal (K_L = 0.12 hours^{-1} W_p^{-1}). W_p^m, which is the starting L-R pyrite concentration in the coal used in each of the above experiments (Table 8, Section 2.4.1), was assumed to be the starting pyrite concentration of the corresponding coals processed at 102°C.

The data in Figure 5 show that the leaching time required to obtain a given S_p removal at 102°C (ambient pressure processing) is five times greater than that required for the same S_p removal at 120°C (L-R processing) provided the leaching took place under identical $\bar{Y}$ values. Thus, the previously estimated five fold increase in K_L value between 102°C and 120°C is further validated. In addition, the data indicate that K_L remains constant up to at least 75-80 percent S_p removal and that the rate of S_p removal depends on the Y value of the reagent during L-R processing just as was proven to be the case with ambient pressure processing (Section 2.4.1). Identical observations were made from similar treatment of 14 mesh coal top size data. It was, therefore, concluded that the K_L values determined in this Section for the L-R processing of the two top size coals at 120°C are valid for up to approximately 80 percent S_p removal. Thus, their use in Equation (3), in conjunction with experimentally derived Y versus t_{L-R} data, should lead to the prediction of the 120°C S_p versus t_{L-R} data in Appendices A and B of Volume 2 regardless of the experimental conditions used to generate these data (except for temperature), provided that Equation (3) is a valid rate expression for L-R processing of suspendable L.K. coal as it has been determined to be for separate leaching-regeneration.

Equation (3) was subjected to the validity test and the results are summarized in Tables 9 (100 mesh top size coal) and 10 (14 mesh top size coal). The test proved conclusively that the rate of pyrite removal from suspendable Lower Kittanning coal during L-R processing is predictable by Equation (3) up to at least 80 percent S_p removal.

TABLE 9. ANALYZED AND PREDICTED PYRITIC SULFUR CONTENT OF 100 MESH TOP SIZE L.K. COAL AS A FUNCTION OF L-R PROCESSING TIME AT 120°C

Exp.	t_{L-R} = 0.5 Hours			t_{L-R} = 1.0 Hours			t_{L-R} = 1.5 Hours			t_{L-R} = 2.0 Hours			t_{L-R} = 3.0 Hours		
No	$\overline{Y}$	S_p^*	$(S_p)_p$	$\overline{Y}$	S_p^*	$(S_p)_p$	$\overline{Y}$	S_p^*	$(S_p)_p$	$\overline{Y}$	S_p^*	$(S_p)_p$	$\overline{Y}$	S_p^*	$(S_p)_p$
A. 3 Wt.% Iron Reagent; 20 wt.% Coal Slurry; 100 psig (85 psi O_2).															
1	.50	1.57	2.16	.60	1.00	1.37	.65	1.06	0.97	.68	1.0±.2	.73		N/A	
2	.39	(2.15)	2.54	.45	2.39	1.87	.51	(2.07)	1.34	.56	1.06	.99	.63	N/A	0.61
3	.45	NA	2.28	.51	(3.00)	1.62	.56	1.05	1.17	.61	1.03	.86	.67	1.0±.3	0.54
4	.50	1.89	2.19	.58	1.41	1.44	.64	0.92	0.99	.68	0.89	74	.74	N/A	0.46
5	.40	1.89	2.48	.47	1.84	1.78	.53	(0.67)	1.27	.59	(0.61)	.91	.67	N/A	0.55
6	.44	2.27	2.54	.51	1.99	1.73	.60	1.21	1.12	.64	(0.61)	.83	.70	N/A	0.52
B. 5 Wt.% Iron Reagent; 20 wt.% Coal Slurry; 100 psig (85 psi O_2).															
7	.61	2.09	1.85	.69	1.2±.1	1.15									
8	.60	2.03	1.92	.69	1.16	1.17	.75	0.7±.1	0.79						
9	.56	2.14	2.04	.67	1.24	1.22	.74	9.94	0.81	.78	0.7±.1	0.59			
10	.39	2.19	2.20	.47	1.68	1.62	.55	1.39	1.16	.60	0.87	0.85	.69	0.8±.1	0.51
11	.44	2.65	2.18	.52	2.10	1.53	.59	1.79	1.07	.67	1.09	0.74	.72	0.81	0.48
12	.66	1.62	1.65	.74	1.24	1.02	.79	(0.60)	0.71	.82	(0.55)	0.53	.86	(0.50)	0.35
C. 5 Wt.% Iron Reagent; 33 Wt.% Coal Slurry; 100 psig (85 psi O_2).															
13	.48	2.30	2.39	.60	1.5±.1	1.44									
14	.44	2.24	2.49	.54	1.62	1.61	.62	1.06	1.06	.69	1.0±.1	0.73			
15	.27	2.72	2.96	.33	2.26	2.39	.40	1.96	1.77	.44	1.68	1.37	.53	1.0±.1	0.80
16	.47	2.03	2.26	.59	1.36	1.41	.67	0.99	0.93	.72	0.77	0.67	.79	(0.66)	0.41
D. 5 Wt.% Iron Reagent; 33 Wt.% Coal Slurry; 50 psig (35 psi O_2).															
17	.49	2.42	2.21	.56	1.56	1.49	.62	1.08	1.04	.67	0.9±.1	0.75			

---

t_{L-R} = L-R processing time; $\overline{Y}$ = Average Y value during the indicated t_{L-R} (experimentally determined; S_p^* = Pyritic sulfur content of coal determined from coal analyses (corrected for errors in organic sulfur value); $(S_p)_p$ = Predicted pyritic sulfur content of coal from leaching rate expression, (Equation 3) with K_L = 0.6 hours^{-1} W_p^{-1}

Values in parentheses are of questionable accuracy. N/A not available.

TABLE 10. ANALYZED AND PREDICTED PYRITIC SULFUR CONTENT OF 14 MESH TOP SIZE L.K. COAL AS A FUNCTION OF L-R PROCESSING TIME AT 120°C (5 WT% Fe REAGENT)

Exp.	t_{L-R} = 0.5 Hours			t_{L-R} = 1.0 Hour			t_{L-R} = 1.5 Hours			t_{L-R} = 2.0 Hours			t_{L-R} = 3.0 Hours		
No.	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$
A. 20 Wt.% Coal Slurries; 100 psig (85 psi O_2).															
23	.71	1.41	1.74	.78	1.12	1.10	.83	0.95	0.77	.86	1.02	0.58	.89	.75±.05	0.39
24	.67	NA	1.85	.76	0.90	1.15	.81	NA	0.80	.84	0.62	0.61	.87	NA	0.41
25	.71	NA	1.76	.78	0.98	1.11	.83	NA	0.77	.86	0.86	0.58	.89	NA	0.39
26	.71	NA	1.75	.78	1.11	1.11	.83	NA	0.77	.86	0.72	0.58	.90	NA	0.38
27	.69	NA	1.82	.76	1.63	1.15	.81	NA	0.80	.84	1.22	0.61	.87	NA	0.41
B. 33 Wt.% Coal Slurries; 100 psig (85 psi O_2).															
28	.48	2.42	2.53	.57	1.5±.1	1.69									
29	.44	2.36	2.59	.51	1.90	1.86	.59	1.5±.1	1.28						
30	.38	(2.31)	2.81	.46	(2.31)	2.06	.54	1.59	1.43	.61	1.0±.1	1.02			
31	.37	3.02	2.89	.44	2.35	2.16	.51	(2.01)	1.54	.57	1.29	1.12	.67	.8±.1	0.65
32	.46	2.29	2.56	.53	1.80	1.80	.60	1.26	1.25	.67	0.86	0.88	.75	0.70	0.53
33	.47	2.17	2.51	.54	1.73	1.76	.62	1.18	1.20	.68	(0.68)	0.86	.77	(0.48)	0.51
C. 33 Wt.% Coal Slurries; 50 psig (35 psi O_2).															
34	.40	3.08	2.88	.52	1.9±.1	1.90									
35	.51	2.23	2.43	.60	1.65	1.60	.66	1.07	1.11	.70	.85±.1	0.83			
D. 33 Wt.% Coal Slurries; 150 psig (135 psi O_2).															
36	.36	(2.17)	2.98	.48	1.70	2.04	.60	1.29	1.28	.67	1.1±.1	0.90			

NA = Not Available (slurry samples were not drawn at these t_{L-R}). Refer to Table 9 for definition of t_{L-R}, $\bar{Y}$, S_p^*, and $(S_p)_p$; K_L = 0.5 hours^{-1} W_p^{-1}

Values in parentheses are of questionable accuracy.

Tables 9 and 10 summarize all of the S_p and Y versus t_{L-R} data generated during the first 3 hours of L-R processing of L.K. coal with iron containing starting reagent at 120°C. The data are divided into five L-R reaction time intervals (t_{L-R}) with the end of each time interval representing a slurry sampling point. The average reagent Y and the experimental and predicted S_p values are listed for each t_{L-R}. Also, the data are grouped with respect to reagent iron concentration, slurry coal content, and oxygen partial pressure. Each $\bar{Y}$ value represents the average reagent Y during the indicated interval and it was computed from plots of the Y versus t_{L-R} data listed in the tables of Appendices A and B. The S_p^* values represent the pyritic sulfur concentration in the coal at the end of each reaction interval; they were derived from sulfur forms analyses of the coal in slurry samples or from analyses on the product coal (the pyritic sulfur value was adjusted for anomalies in the organic sulfur content of the coal sample). The $(S_p)_p$ values represent the predicted pyritic sulfur content of the coal at the end of each t_{L-R} as computed from

$$(S_p)_p = \left(\frac{64.1}{120}\right) / \left(K_L \bar{Y}^2 t_{L-R} + \frac{1}{W_p^m}\right) \qquad (12)$$

Equation (12) is an integrated form of Equation (3); all of its terms have been defined previously. The values of K_L, $\bar{Y}$, and t_{L-R} are listed in Tables 9 and 10; the values of W_p^m for each experiment are listed in Table 8 (Section 2.4.1).

Comparison of analyzed and predicted S_p values in Tables 9 and 10 reveals good agreement in these majority of cases; in fact, when normal sampling and analyses uncertainties are taken into consideration the agreement can be considered excellent for S_p removals up to nearly 80 percent (residual S_p 0.8 wt. percent). It should be noted that these experimental data were generated under a variety of processing conditions involving starting reagent iron and sulfate concentrations, starting reagent Y, slurry coal content, slurry pH, total pressure, and oxygen partial pressure.

The large majority of the S_p^* values in Tables 9 and 10 were derived from analyses of coal present in reactor samples drawn during processing. The S_p^* values for which a deviation is indicated represent analyses performed on samples taken at the end of the run where the entire batch of L-R processed coal was sampled; the deviation was derived either from duplicate analyses on the same sample or from analyses of duplicate samples. S_p^* values which appeared to be grossly inconsistent with respect to the rest of the data derived from a particular experiment or with respect to data from similar experiments are placed in parentheses in the above tables. Discrepancies between analyzed and predicted S_p are not limited to the values in parentheses; in certain cases, entire experiments appear not to obey Equation 3 (e.g., Experiments 2 and 11), but the reasons for the discrepancy are not readily apparent.

The majority of the discrepancies between analyzed and predicted S_p appear in the first group of experiments in Table 9 (Experiments 1 through 6). In these experiments coal was processed with iron sulfate solutions which did not contain added sulfuric acid. Apparently, without the added acid the pH during L-R processing was not sufficiently low to inhibit iron sulfate deposition on the coal (see data in Appendix A, Table A-1). It is conceivable that the deposited iron sulfate complicated the sulfur forms analyses performed on these coal samples and led to errors in pyritic sulfur determinations (10 to 20 percent error in pyritic sulfur analyses can account for most of the observed discrepancies). Another reason that the discrepancies between analyzed and predicted S_p are concentrated in this group of experiments may be inadequate sampling. Experiments 1 through 6 represent early experimentation with L-R processing and it could be that sampling techniques were not as good as later in the program. It should be noted, however, that there is nothing in this group of data, or in any of the other groups of data in Tables 9 and 10, which relates discrepancies between analyzed and predicted S_p values to the value of a certain processing parameter (at least within the indicated ranges of the processing parameters).

Consistent discrepancies between predicted and analyzed S_p values appear when the pyritic sulfur concentration in coal has been reduced to approximately 0.8 weight percent (nearly 80 percent pyrite removal). Apparently, further S_p reduction during L-R processing takes place at rates which are appreciably lower than those predicted by Equation (3) and the K_L values in Tables 9 and 10. This discrepancy between S_p^* and $(S_p)_p$ becomes more apparent when predicted S_p values for three hours L-R processing (Tables 9 and 10) are compared to S_p values derived from analyses of coal processed in excess of three hours (Experiments 2, 4, 5, 6, 11, 12, 16, 24 through 27, 32, and 33 in Appendices A and B, Volume 2). It is also illustrated by the 14 mesh top size data in Figure 6 (120°C rate data from Appendix B).

In Figure 6 the reciprocal pyritic sulfur concentration in coal (coal analysis values corrected for organic sulfur anomalies) is plotted against L-R reaction time which was normalized for inconsistencies in reagent regeneration. According to Equation (12), the slope of the data in Figure 6 should be constant and proportional to the K_L value of Equation (3) for 120°C processing of 14 mesh top size coal. Indeed, the data illustrates that this is the case up to the $1/S_p$ value of approximately 1.2 (S_p of 0.83 wt. percent and W_p of 1.56 wt. percent), but a definite change in K_L value occurs thereafter. Actually, a change in reaction mechanism is indicated by the data which Equation (3) did not predict (speculation on possible causes of data unpredictability in this S_p region and potential modifications of Equation (3) which could possibly rectify this discrepancy were presented in the previous Section). However, in the absence of a more precise rate expression, Equation (3) can be utilized to predict L-R processing even beyond 80 percent pyrite removal by allowing for a change in the isothermal value of K_L.

The data in Figure 6 indicate that L-R processing can best be represented by Equation (3) through the use of three K_L values. For the 14 mesh top size L.K. coal processed at 120°C the indicated K_L values are as follows:

$$K_{L1} = 0.5\ (\text{hours})^{-1}\ (\%\ \text{pyrite in coal})^{-1}\ \text{for}\ W_p \geq 1.6\ \text{wt.\%}$$

$$K_{L2} = f(W_p) = W_p - 1.1\ (\text{hours})^{-1}\ (\%\ \text{pyrite})^{-1}\ \text{for}\ 1.6 \geq W_p \geq 1.2\ \text{wt.\%}$$

$$K_{L3} = 0.1\ (\text{hours})^{-1}\ (\%\ \text{pyrite in coal})^{-1}\ \text{for}\ W_p \leq 1.2\ \text{wt.\%}$$

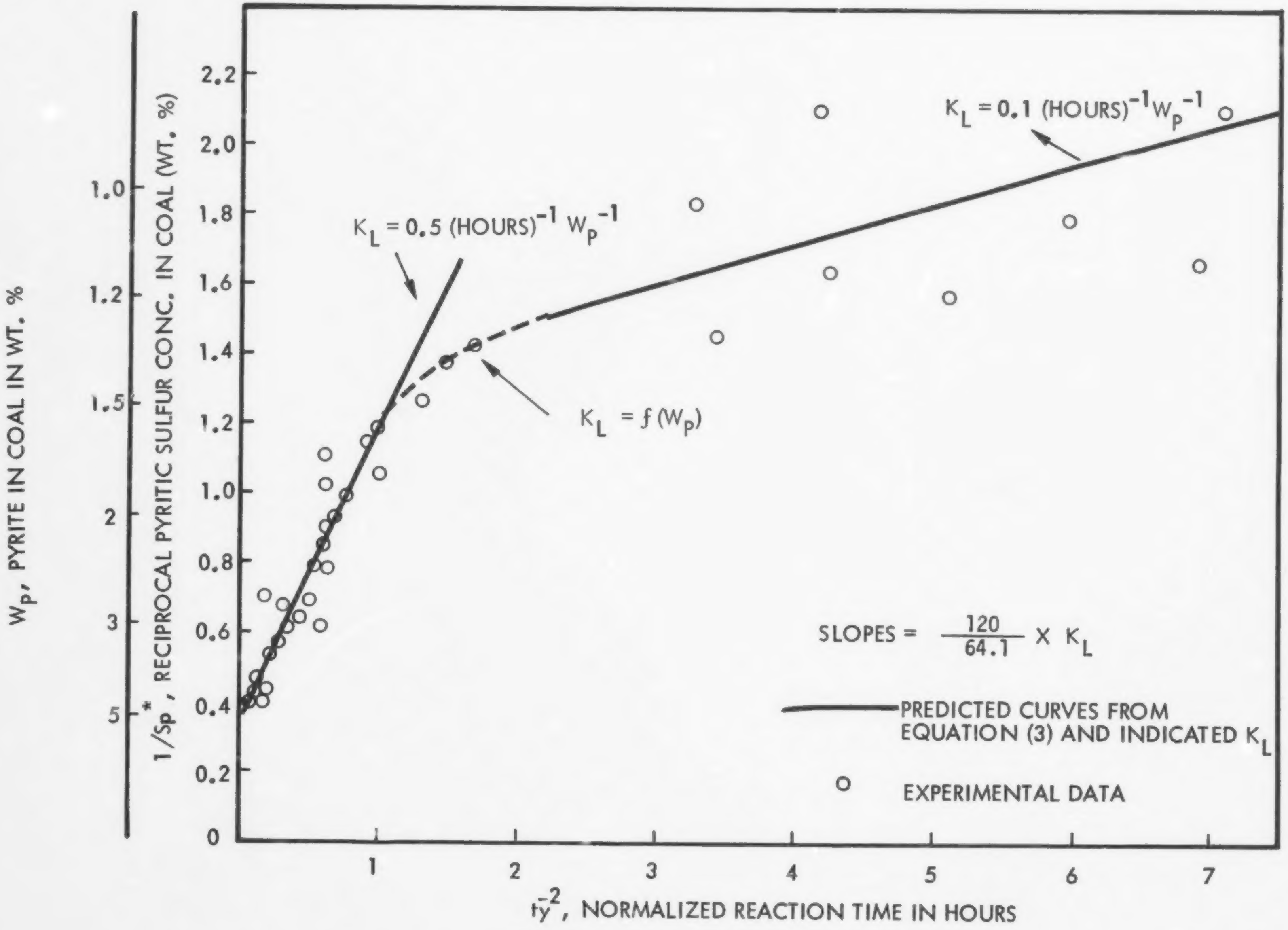


Figure 6. Pyrite Leaching Rate Constant Data

The deviation in the K_{L1} is estimated to be ± 10 percent, but the deviation in the K_{L3} value is closer to ± 50 percent. However, the large deviation in K_{L3} is understandable since it can result from only a ± 0.1 deviation in the S_p values which comprise the concentration region to which K_{L3} applies; such deviation is normal for pyritic sulfur analyses.

It is interesting to note that the estimated K_{L3} value is identical to the K_L value found applicable for ambient pressure processing of the same size coal at 102°C. Within experimental uncertainty, the same observation was made with the 100 mesh top size coal where K_{L3} was estimated to be 0.12 $(\text{hours})^{-1}$ $(W_p)^{-1}$.* The implication of this observation is that if K_{L3} is temperature insensitive during small temperature changes (e.g., a diffusion constant) it is possible to have an observable change in reaction mechanism at 120°C but not at 102°C, provided that at 102°C K_{L1} and K_{L3} are nearly identical. This may be the case with suspendable L.K. coal since the L.K. coal used in the previous bench-scale program indicated no change in the pyrite leaching rate mechanism up to 95 percent pyrite removal at 102°C (see also discussion in Section 2.4.1).

It is believed that the preceding discussion proves conclusively that Equation (3) can be used to predict the Meyers Process performance during the L-R processing of suspendable L.K. coal at 120°C provided the experimentally derived K_L values are used and the Y versus t_{L-R} history of the process is known. The latter requirement limits the utility of Equation (3) severely unless the change in Y during L-R processing can be predicted through the use of a valid reagent regeneration rate expression. In the next Section an attempt is made to prove that Equation (5) is the appropriate reagent regeneration rate expression for L-R processing when oxygen supply to the slurry is adequate and proper mixing has occurred.

---

*The K_{L1} for 100 mesh top size coal was determined earlier to be 0.6 $(\text{hours})^{-1}$ $(W_p)^{-1}$; the K_{L2} was estimated to be the same as that of the 14 mesh top size coal.

2.4.2.2 Reagent Regeneration During L-R Processing

Reagent regeneration involves the oxidation of the Fe^{+2} generated during the pyrite leaching reaction to Fe^{+3} by oxygen. During L-R processing the two operations (pyrite leaching-reagent regeneration) take place simultaneously and their rates are related through the iron forms in the reagent. The regeneration rate depends on the Fe^{+2} concentration in the reagent solution and the leaching rate on the Fe^{+3}-to-Fe ratio, which is defined as Y.* Since Fe^{+3} is equal to $Fe-Fe^{+2}$, Y is also a measure of regeneration rate.

Review of the Y versus t_{L-R} data in Appendices A and B, Volume 2 reveals that in most experiments the rise in Y was rapid during the early stages of L-R processing. This observation during the performance of the experiments led to the erroneous conclusion that reagent regeneration was taking place efficiently during L-R processing. When valid pyrite leaching rate constants were determined, it became possible to generate predicted Y versus t_{L-R} data which when compared to the experimental data led to the following observations:

- In the majority of experiments reagent regeneration was less efficient than predicted during the first hour of L-R processing.
- Reagent regeneration was inconsistent in a number of experiments.
- Equations (5) and (6) appeared to be valid rate expressions for spent reagent regeneration, but the activation energy value computed from the regeneration of synthetic spent reagents for use in Equation (6) is probably higher than the activation energy applicable to the regeneration of actual spent reagent in the presence of coal.
- The reagent regeneration rate was probably catalyzed by cations leached from the coal[4] or by the coal itself.

---

*Note that because of Fe^{+2} production in the mixer the starting L-R Y was always low; therefore, high regeneration rates were expected during the early stages of L-R processing.

The validity of the above observations becomes evident from the data presented in Figures 7 through 9 where predicted Y versus t_{L-R} data (solid curves) are compared to measured Y values as a function of L-R processing time (dashed curves). The predicted data in these figures was abstracted from Table D-1, Appendix D, Volume 2 of this report.

Table D-1 lists predicted data for both the Mixer and L-R Operations which correspond to the experimental data from every experiment in Appendices A and B of Volume 2. The data for each experiment are presented in two sections. The top section lists Mixer Operation data which were discussed in detail in Section 2.4.1. The bottom section lists the predicted W_p (pyrite concentration in coal), Y, and x_{L-R} (fraction of pyrite removed during L-R) as a function of t_{L-R} (L-R reaction time); it also lists the overall pyrite removal, x_{tot}, at each of the t_{L-R} values shown (overall pyrite removal is based on starting coal W_p and it includes pyrite removal in both the Mixer and L-R Operations). The predicted L-R data were generated from known starting coal and reagent compositions and Equations (3), (5), and (6). The K_L values used in Equation (3) were those determined as applicable to L-R data up to 80 percent pyrite removal. The K_R values (regeneration rate constants) were computed from the Arrhenius constants, A_R and E_R, through the use of Equation (6); these constants were determined from synthetic spent reagent solutions.

Figure 7 illustrates measured and predicted Y values derived from L-R processing at 120°C of 20 wt. percent slurries of 100 mesh top size L.K. coal. The solid curve depicts the expected Y variation with L-R reaction time from Experiments 8 through 12 (predicted data) and the dashed curves show the corresponding experimentally derived Y data. If small differences in starting Y values and Mixer reaction times are disregarded, the only meaningful difference among these experiments was L-R reaction time. Thus, at any given reaction time the slurry composition, and therefore Y, should be the same for all the experiments in this group (a small variation could be explained on the basis of the observed differences in starting L-R Y values). The predicted data curve confirms that these experiments should have yielded identical Y versus t_{L-R} data if performed reproducibly. The

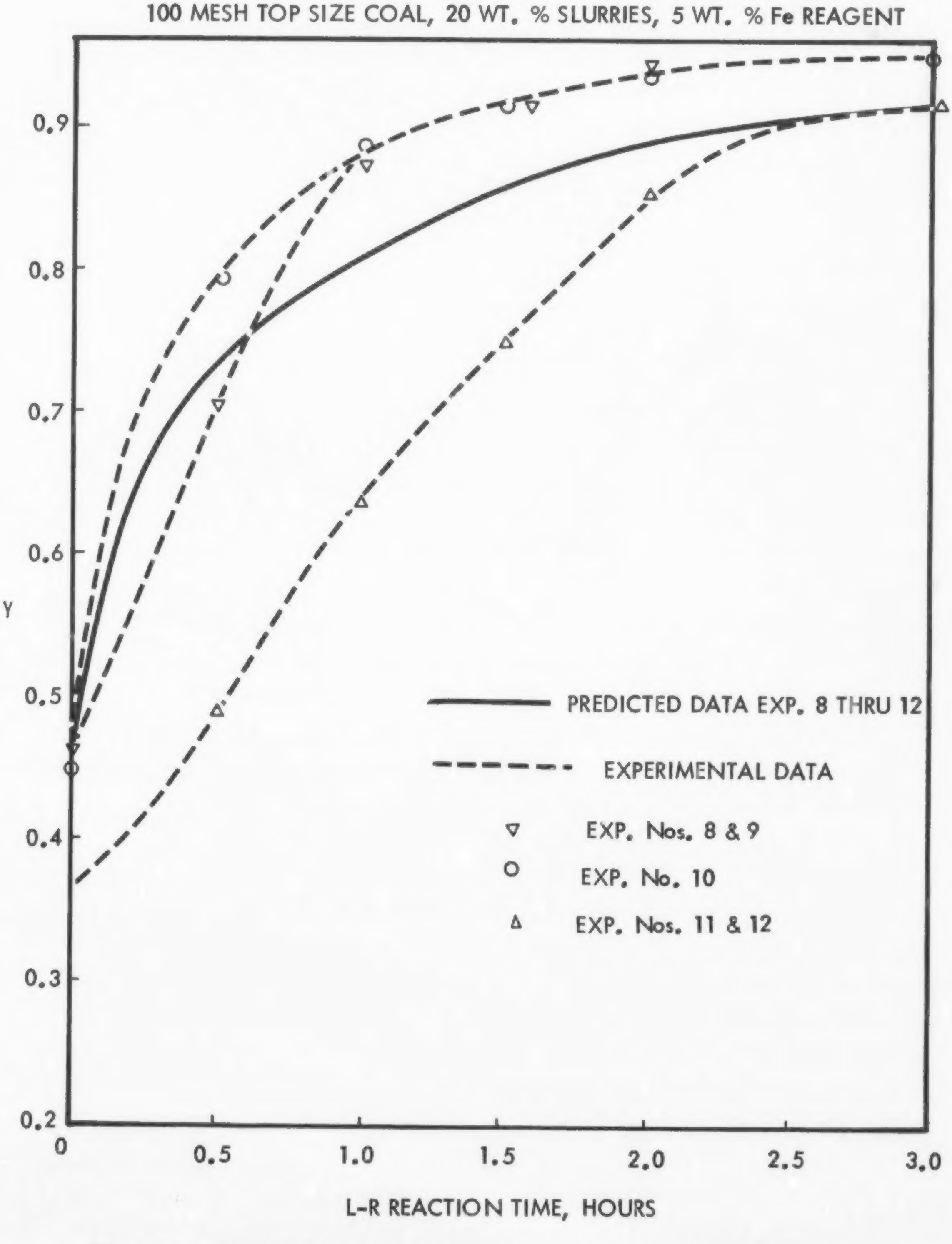


Figure 7. Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 120°C

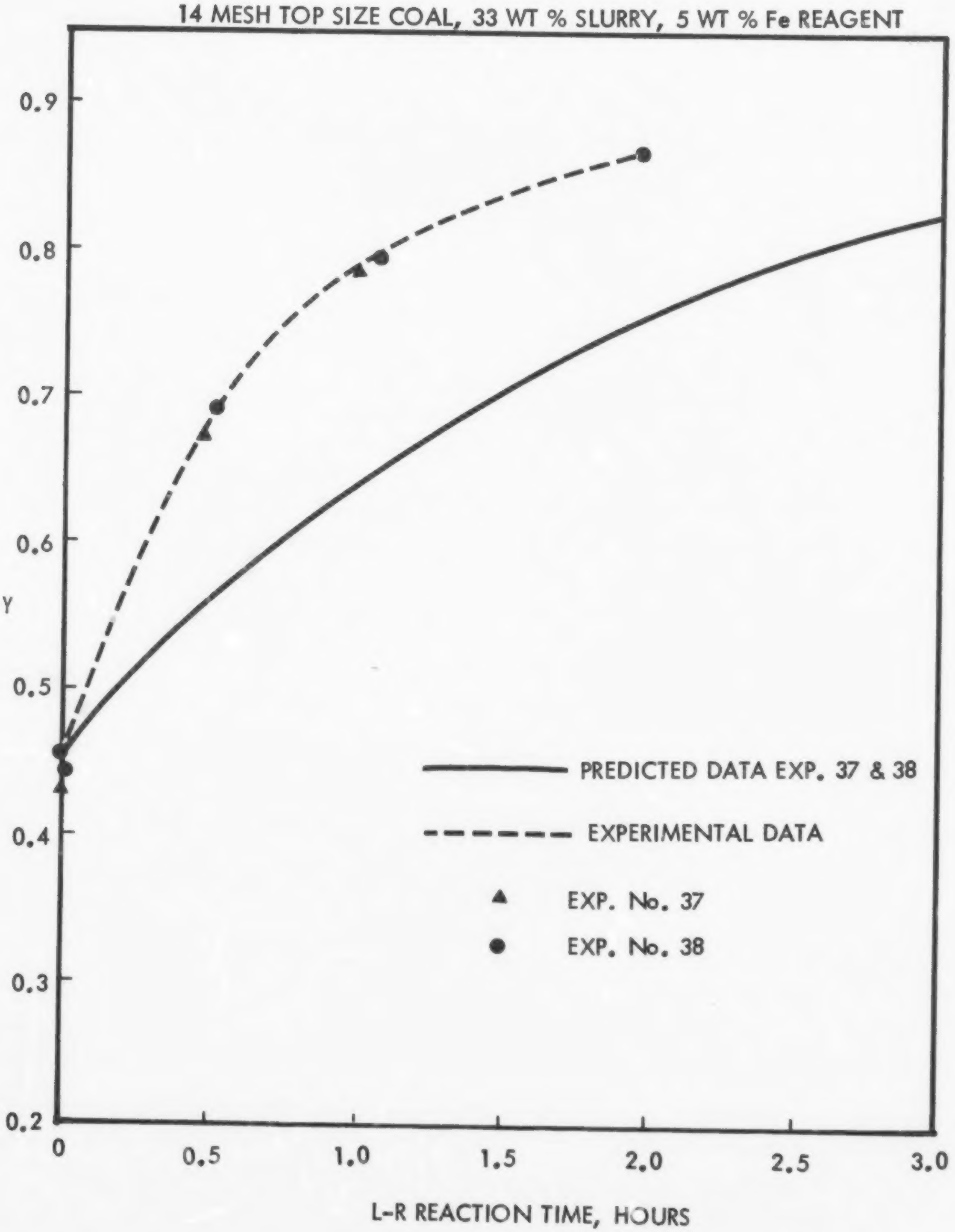


Figure 8. Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 110°C

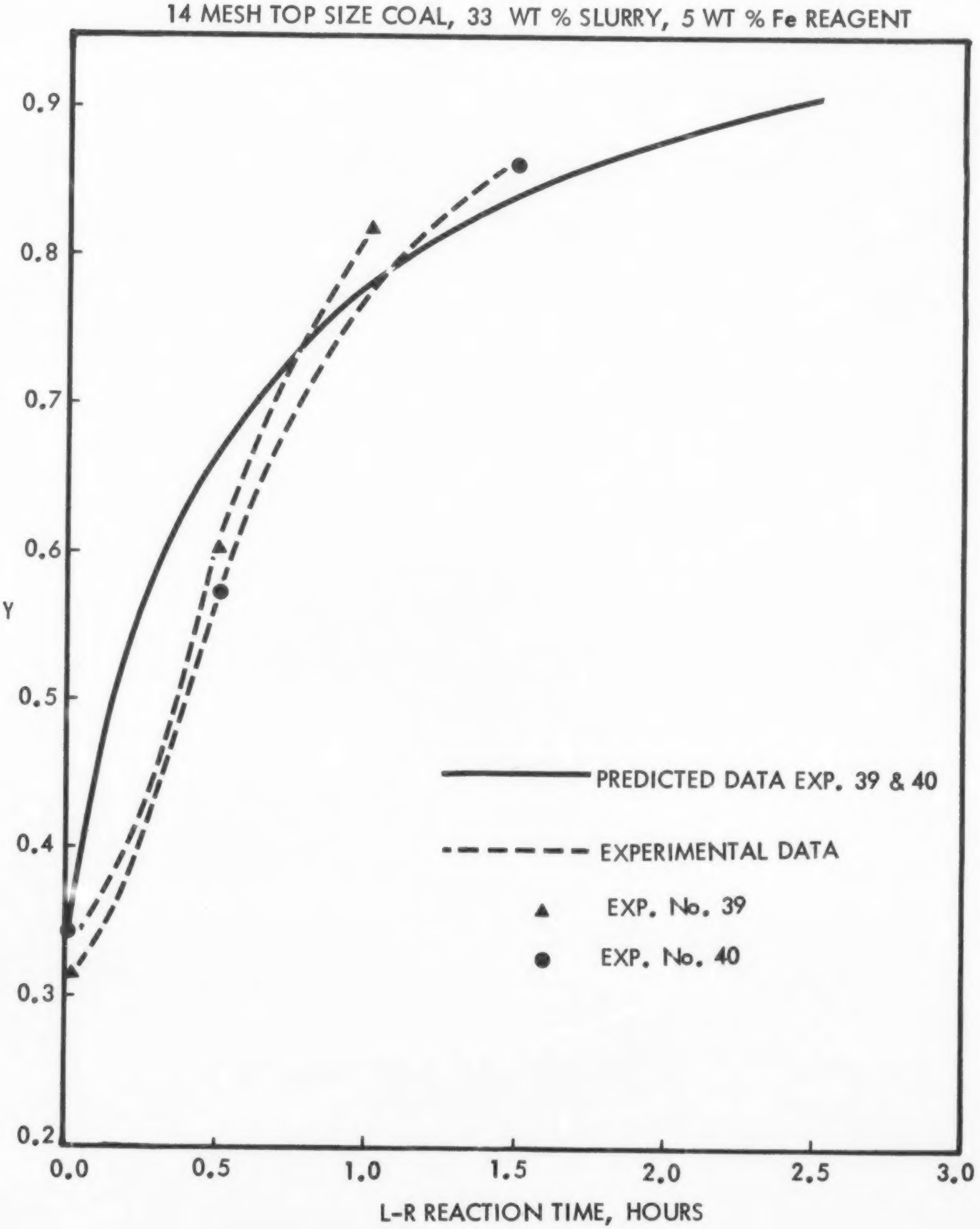


Figure 9. Predicted and Experimental Y Values During L-R Processing of L.K. Coal at 130°C

experimental data show that Experiments 8 and 9 yielded reproducible data which, however, differed substantially from the data generated in Experiment 10 or in Experiments 11 and 12. The lack of consistency in Y data reproducibility could have only resulted from inconsistent oxygen supply to the slurry (insufficient feed or inefficient mixing) since there was no evidence of errors in iron mass balance. (Note that the Y value depends only on Fe^{+2} and oxygen concentration when pyrite leaching is performed at constant temperature; starting Y has a negligible effect as indicated by the predicted curve in Figure 7).

As would be expected from inefficient regeneration, the data in Figure 7 reveal that oxygen starvation was more pronounced during the early stages of L-R processing when Fe^{+2} generation was high; however, the data also reveal that oxygen starvation need not have taken place if experimentation was performed in accordance with the procedures used in Experiment 10.* In Experiment 10 the oxygen supply to the slurry appears to have been adequate to permit reagent regeneration to take place under the kinetically controlled rate. This conclusion is based on the observation that the experimental Y versus t_{L-R} data from this experiment traces a curve which is identical in shape to the predicted curve (the two curves will coincide if translated on the time axis by a constant multiplier). Conversely, this observation leads to the conclusion that Equation (5) is a valid reagent regeneration rate expression for use in the prediction of L-R processing data. The fact that the predicted and measured reaction times for the same Y value differs by a constant factor indicates that the actual K_R value for this temperature is higher than that used in Equation (5) to generate the predicted data curve. Since Equation (6) is also probably valid on the basis of the above data comparisons, a wrong K_R value implies that at least one of the Arrhenius constants used to predict the L-R data was wrong.

Equations (5) and (6) were derived from a substantial bank of data on the regeneration of synthetic spent reagent solutions (previous bench-scale program). It is highly unlikely that the Arrhenius constants determined from these experiments were wrong. It was, therefore, assumed that the apparent higher K_R values observed here under L-R processing were due to catalytic effects emanating from some unknown substance leached from the coal (probably metallic cations and very likely copper).* The catalytic effect would be expected to manifest itself through the lowering of the activation energy of the reaction, higher K_R values, and different, most likely lower, K_R dependence on temperature. In fact, if the A_R value was not affected by the catalyst, it would be expected that the catalytic effect on K_R to be proportionally greater at the lower of two reaction temperatures. The data in Figures 7, 8, and 9 tend to show that this was actually the case. Until further verified, this catalytic effect should be considered as an assumption.

---

*Oxygen feed procedures were not intentionally varied, but precise control of slurry circulation rates was difficult in the experimental set-up used in this program, principally because of slurry pump size.

In Figure 8, predicted data are compared to experimental L-R data generated at 110°C. In Figure 9, the same type of data are compared from 130°C experimentation. In both cases experimentation involved the L-R processing of 14 mesh top size L.K. coal as 33 wt. percent slurries in 5 wt. percent iron reagent. Very good reproducibility of data is exhibited by each pair of experiments depicted in these two Figures. However, it appears that the regeneration rate did not reach its kinetic limits during at least the first hour of L-R processing at 130°C probably due to insufficiency in oxygen. Thus, the 130°C experimental curves in Figure 9 are not expected to obey Equation (5) and, therefore, they are not strictly comparable to the data from Experiment 10 (Figure 7) and Experiments 37 and 38 (Figure 8). Yet it can still be argued that the delta between "catalyzed" and "uncatalyzed" K_R values is smaller at the lower temperatures (this is especially true if it is assumed the regeneration rate at t_{L-R} = 1.5 hours is no longer limited by oxygen). Of course, the effect of temperature on the difference in predicted and experimental (suggested from measured Y) K_R values is readily apparent from comparison of the data in Figures 7 and 8.

Predicted and experimental data were compared for all the experiments in Appendices A and B. (The experimental Ys are listed in Appendices A and B and the corresponding predicted Ys in Appendix D). These comparisons strengthened further the conclusions drawn from the data in Figures 7 through 9. However, the number of experiments during which regeneration was not limited by oxygen insufficiency was small and, therefore, no attempt was made to estimate either the activation energy of the assumed catalyzed reaction or the K_R value at any given L-R temperature. Attempts to discern any variation in the K_R value as a function of reagent recycle time (due to accumulation of catalyst) were inconclusive for the same reason.

---

*It is possible, but not very probable, that the catalyst was leached from the reactor, since different type stainless steel reactors were used during L-R and synthetic reagent experimentation.

The above analysis on the reagent regeneration data derived from L-R processing furnishes the reasons for (a) the scatter in the pyrite removal versus leaching time data, (b) the difficulty to discern any sensitivity in pyrite removal rates to changes in processing parameters, and (c) the requirement that experimental and not predicted Y values had to be used in Equation (3) in order to predict the generated S_p versus t_{L-R} data. Thus, it became clear that parametric effects on pyrite leaching must be examined on the basis of predicted data rather than experimental data in order that the real effect of each parameter becomes apparent. Since Equation (3) was proven to be a valid leaching rate expression under virtually all processing conditions examined when experimentally determined K_L values were used with it (Section 2.4.2.1) and since Equations (5) and (6) appeared to be valid on the basis of the data analysis performed in this section, the predicted data listed in Table D-1, Appendix D, Volume 2 were used wherever appropriate in the examination of parametric effects. It should be noted, however, that the data in Table D-1 are only valid up to 80 percent pyrite removal because they were generated with K_L values which were proven valid only up to this level of pyrite removal. Also, these data were generated using A_R and E_R values derived from uncatalyzed reagent regeneration reactions; thus, the predicted pyrite removal values listed in Table D-1 are lower than the expected pyrite removal values from L-R processing under efficient reagent regeneration. However, at a given L-R processing temperature these values are uniformally lower and should not affect data comparison.

The higher (uncatalyzed) E_R value was also used in process engineering analysis because the lower ("catalyzed") E_R value could not be determined with adequate precision from the available data and because it is not known if similar E_R depression would occur during the L-R processing of other coal, even L.K. coals from different mine than the one used in the current program. The use of the higher E_R value should not substanially affect the size of the reactors or the computed process costs, except perhaps when L-R operation is performed at low temperatures and pressures (e.g., 100°C and 50 psig).

2.4.2.3 Temperature Effects on L-R Processing of L.K. Coals

Figures 10 and 11 illustrate the temperature effect on pyrite removal during the L-R processing of 100 and 14 mesh top size L.K. coals in the temperature range of 110°C to 130°C. The temperature effect was investigated on 20 wt. percent slurries of 100 mesh coal and on 33 wt. percent slurries of 14 mesh coal; thus, the data plotted in these figures differ in two processing variables. However, the temperature effect should be identical for the two top size coals and, therefore, the observed difference in the magnitude of the temperature effect in Figures 10 and 11 is entirely due to the difference in slurry concentrations.*

The data in Figures 10 and 11 show that the rate of pyrite removal from suspendable L.K. coals during L-R processing increases with increasing temperature. In addition, the temperature effect on pyrite removal is larger between 110° and 120°C than between 120° and 130°C regardless of slurry composition and it is more pronounced on 33 wt. percent slurries than on 20 wt. percent slurries. The data also reveal that the 130°C curves of the two slurry concentrations are nearly identical. These observations lead to the conclusion that in terms of temperature effect alone, the most efficient processing conditions, among those represented in Figures 10 and 11, are the conditions under which Experiment 40 was performed. In addition, the data in these figures indicate that 33 wt. percent slurry processing is preferable to 20 wt. percent slurry processing at any of the three temperatures since twice as much coal per unit time is processed at

---

*Pyrite removal rates from the two size fraction coals differ only in A_L value (Arrhenius frequency factor) which is temperature independent.

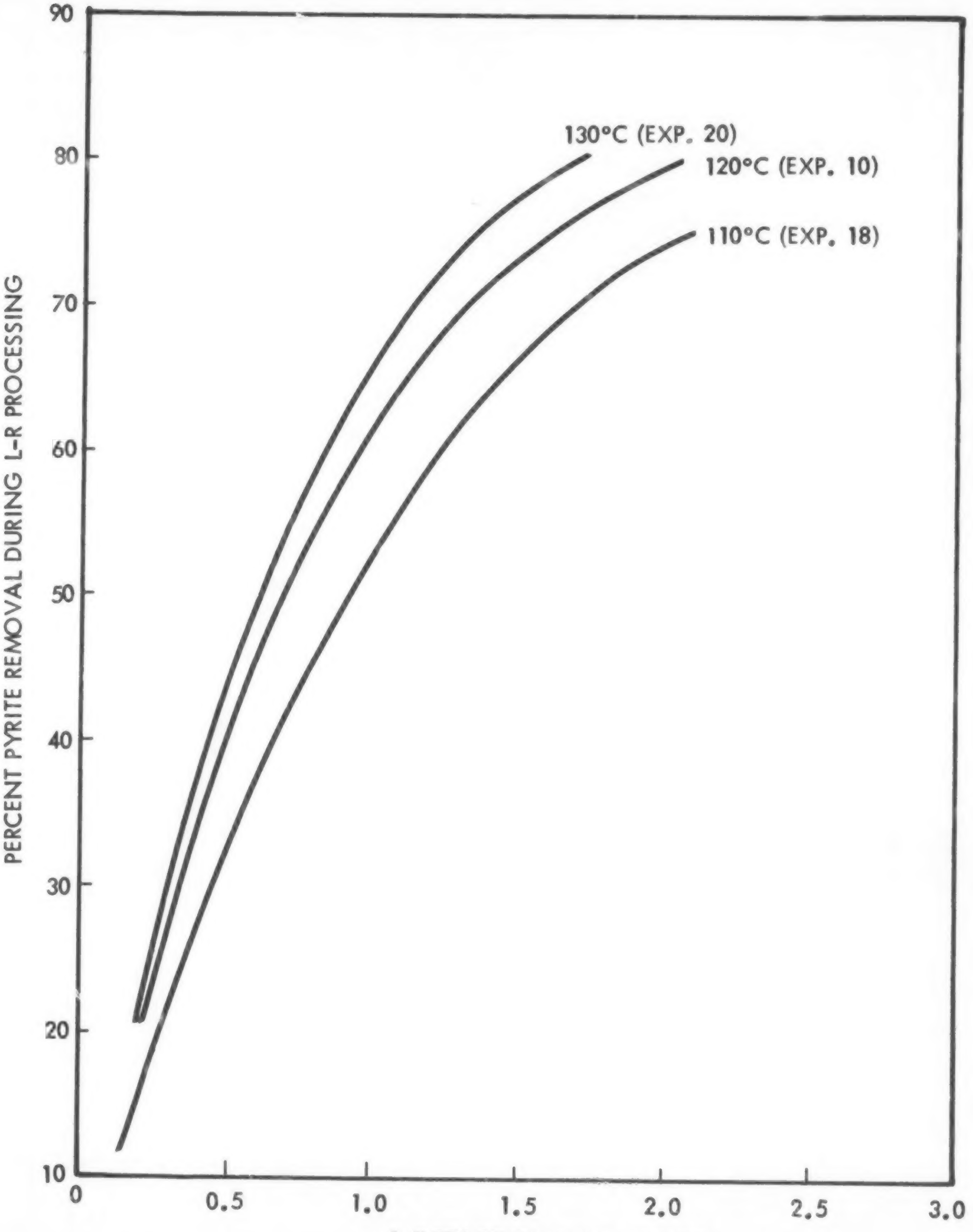


Figure 10. Temperature Effect on L-R Processing of 100 Mesh Top Size L.K. Coal (20 Wt. Percent Slurries)

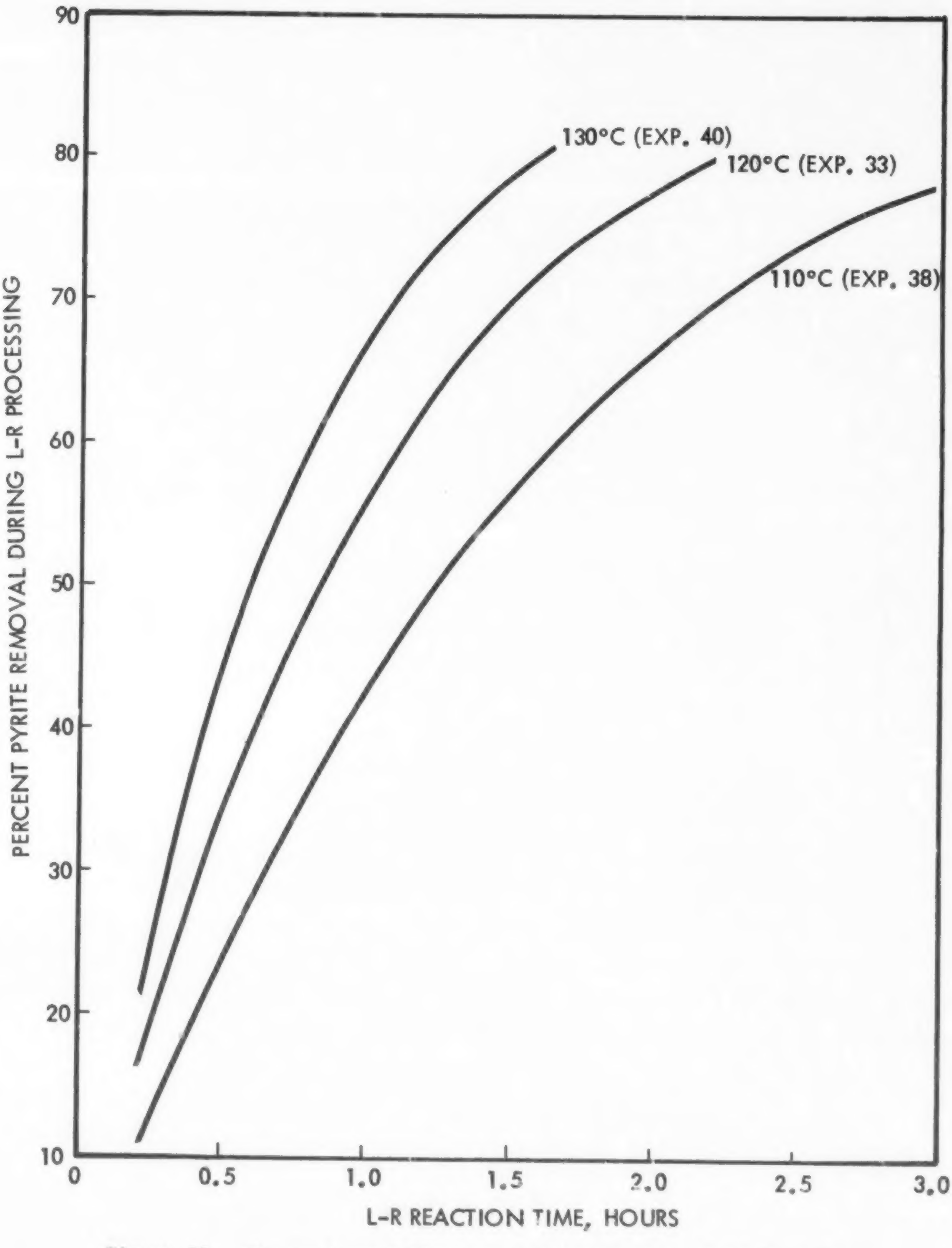


Figure 11. Temperature Effect on L-R Processing of 14 Mesh Top Size L.K. Coal (33 Wt. Percent Slurries)

the higher slurry concentration than at the lower one while the penalty in reaction time for processing the more concentrated slurry never exceeds a factor of 1.5 when comparison is made at the same temperature.

It should be noted that the discussed temperature effects apply only up to 80 percent pyrite removal; beyond this pyrite removal level the temperature effect on L-R processing becomes negligible. Also, the effects depicted in Figures 10 and 11 represent the overall temperature influence on suspendable coal desulfurization during L-R processing and not the dependence on temperature of the individual rates controlling the process pyrite leaching and reagent regeneration.

The temperature effect on the reagent regeneration rate during L-R processing is adequately defined through Equation (6) using the A_R and E_R values listed in Section 2.4.2. It will be shown that the temperature effect on the pyrite leaching rate, up to 80 percent pyrite removal, can also be defined by an Arrhenius type expression, but with at least one of the Arrhenius constants being different for ambient pressure processing from that for L-R processing. Beyond 85 percent pyrite removal the leaching rate appears to be insensitive to temperature in the 102° to 130°C range. A rate constant transition region occurs between 80 and 85 percent pyrite removal, but the leaching rate temperature dependence in this region was not defined.

The inability to predict the values of L-R leaching rate constants from the A_L and E_L values estimated from ambient pressure processing of L.K. coals (see Mixer Section) necessitated that empirical L-R K_L values be determined for each top size coal from L-R data generated at each of the three temperatures. The methodology used to determine these K_L values was described in detail in Section 2.4.2.1 in conjunction with the determination of K_L values for the 120°C L-R processing of 100 mesh and 14 mesh top size L.K. coals. Using this approach the following K_L values were estimated for 110°C and 130°C processing of suspendable L.K. coal:

(a) 110°C L-R Processing

K_L = 0.42 $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$ for 100 mesh top size coal

K_L = 0.35 $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$ for 14 mesh top size coal

(b) 130°C L-R Processing

K_L = 0.84 $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$ for 100 mesh top size coal

K_L = 0.70 $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$ for 14 mesh top size coal

These K_L values were determined from randomly selected experimental data points and subsequently tested through Equation (12) (an integrated form of the leaching rate expression Equation 3) against all the rate data generated at these temperatures (Tables A-5, A-6, B-5, and B-6 in Volume 2). The results of this test are shown in Table 11. The agreement between coal pyritic sulfur content values derived from coal sample analyses, S_p^*, and those predicted by Equation (12), $(S_p)_p$, is, in general, very good. Thus, the K_L values listed above appear to be valid (detailed discussion on the validity of these comparisons was presented in Section 2.4.2.1 in conjunction with the review of the data in Tables 9 and 10).

It is noted that the K_L values for 130°C leaching are exactly double those for 110°C leaching. A factor of 2 was also estimated to be the difference in K_L values for ambient pressure pyrite leaching at temperatures differing by 20°C. This observation implies that the apparent activation energies governing the leaching reaction rates at ambient pressures and under L-R conditions are the same. However, the K_L values between 102°C (ambient pressure) and 110°C (L-R processing) differ by a factor of 3.5. This unexpectedly large factor is not derivable from the A_L and E_L values listed on page 45.

TABLE 11. ANALYZED AND PREDICTED S_p OF L.K. COAL AS A FUNCTION OF L-R PROCESSING TIME AT 110°C (94 PSI O_2) AND 130°C (76 PSI O_2)

Exp.	t_{L-R} = 0.5 Hours			t_{L-R} = 1.0 Hour			t_{L-R} = 1.5 Hours			t_{L-R} = 2.0 Hours			t_{L-R} = 3.0 Hours		
No.	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$	$\bar{Y}$	S_p^*	$(S_p)_p$
A. 100 Mesh Top-Size Coal; 20 Wt.% Slurry; 5 Wt.% Fe Reagent; 110°C.															
18	.55	2.66	2.39	.60	2.18	1.72	.65	1.43	1.25	.70	1.02	0.93	.76	.85±.1	0.60
19	.56	2.57	2.34	.62	2.22	1.65	.67	1.57	1.20	.71	1.01	0.91	.77	0.83	0.59
B. 14 Mesh Top-Size Coal; 33 Wt.% Slurry; 5 Wt.% Fe Reagent; 110°C.															
37	.58	2.33	2.57	.67	1.8±.1	1.74									
38	.61	2.22	2.47	.69	1.69	1.68	.74	1.21	1.22	.77	1.3±.3	0.94			
C. 100 Mesh Top-Size Coal; 20 Wt.% Slurry; 3 Wt.% Fe Reagent; 130°C.															
20	.31	1.87	2.31	.40	1.55	1.64	.48	1.18	1.11	.55	1.0±.1	0.76			
21	.42	1.93	2.08	.54	1.23	1.25	.62	(0.70)	0.80	.67	(0.42)	0.57	.73	(1.0±.1)	0.35
D. 14 Mesh Top-Size Coal; 33 Wt.% Slurry; 5 Wt.% Fe Reagent; 130°C.															
39	.46	2.07	2.30	.60	1.3±.1	1.30									
40	.44	2.35	2.43	.57	1.40	1.41	.65	0.91	0.90	.71	0.9±.1	0.62			

Values in parentheses are of questionable accuracies.

t_{L-R} = L-R processing time; $\bar{Y}$ = Average Y value during the indicated t_{L-R} (experimentally determined); S_p^* = Pyrite sulfur content of coal determined from coal analyses (corrected from errors in organic sulfur value); $(S_p)_p$ = Predicted pyrite sulfur content of coal from Equation 12 (integrated form of pyrite leaching rate expression, Equation 3); K_L values at 110°C: 0.35 and 0.42 $(\text{hours})^{-1}$ $(W_p)^{-1}$ for 14 and 100 mesh top size coals, respectively; K_L values at 130°C: 0.70 and 0.84 $(\text{hours})^{-1}$ $(W_p)^{-1}$ for 14 and 100 mesh top size coals, respectively.

Figure 12 is an Arrhenius plot of K_L values derived from both L-R and ambient pressure processing of suspendable L.K. coals. The ambient pressure curve and the Arrhenius constants derived from it were discussed in Section 2.4.1. In contrast to the ambient pressure processing data, the L-R data exhibit very good compliance to the Arrhenius Equation in the investigated range. The Arrhenius constants derived from these data were as follows:

(a) For 100 mesh top size coal

E_L = 11.1 Kcal/mole pyrite removed

$A_L = 8.9 \times 10^5$ $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$

(b) For 14 mesh top size coal

E_L = 11.1 Kcal/mole pyrite removed

$A_L = 7.4 \times 10^5$ $(\text{hours})^{-1}$ $(\text{pyrite conc. in coal})^{-1}$

2.4.2.4 Coal Top Size Effects During L-R Processing

In previous sections it was demonstrated that the effect of coal top size on suspendable L.K. coal desulfurization by the Meyers Process could be confined to the leaching rate constant. It was also shown that the K_L value of the 100 mesh top size coal was 20 percent larger than that of the 14 mesh coal, regardless of process operating conditions. This delta in K_L values represents the predicted maximum coal particle size effect on pyrite leaching rates when the above two top size coals are processed identically.

Under L-R processing, assuming identical starting systems, the coal top size effect is tempered by the fact that the Y value of the coarser coal slurry at a given reaction time is higher than the Y of the less coarse coal slurry (this is because the finer coal reacts at a higher rate generating more Fe^{+2} and the difference in Fe^{+2} is not entirely compensated by the higher regeneration rate). Figure 13 illustrates the coal top size effect on L-R processing efficiency of suspendable L.K. coal with typical L-R data abstracted from Table D-1, Volume 2. It can be concluded from

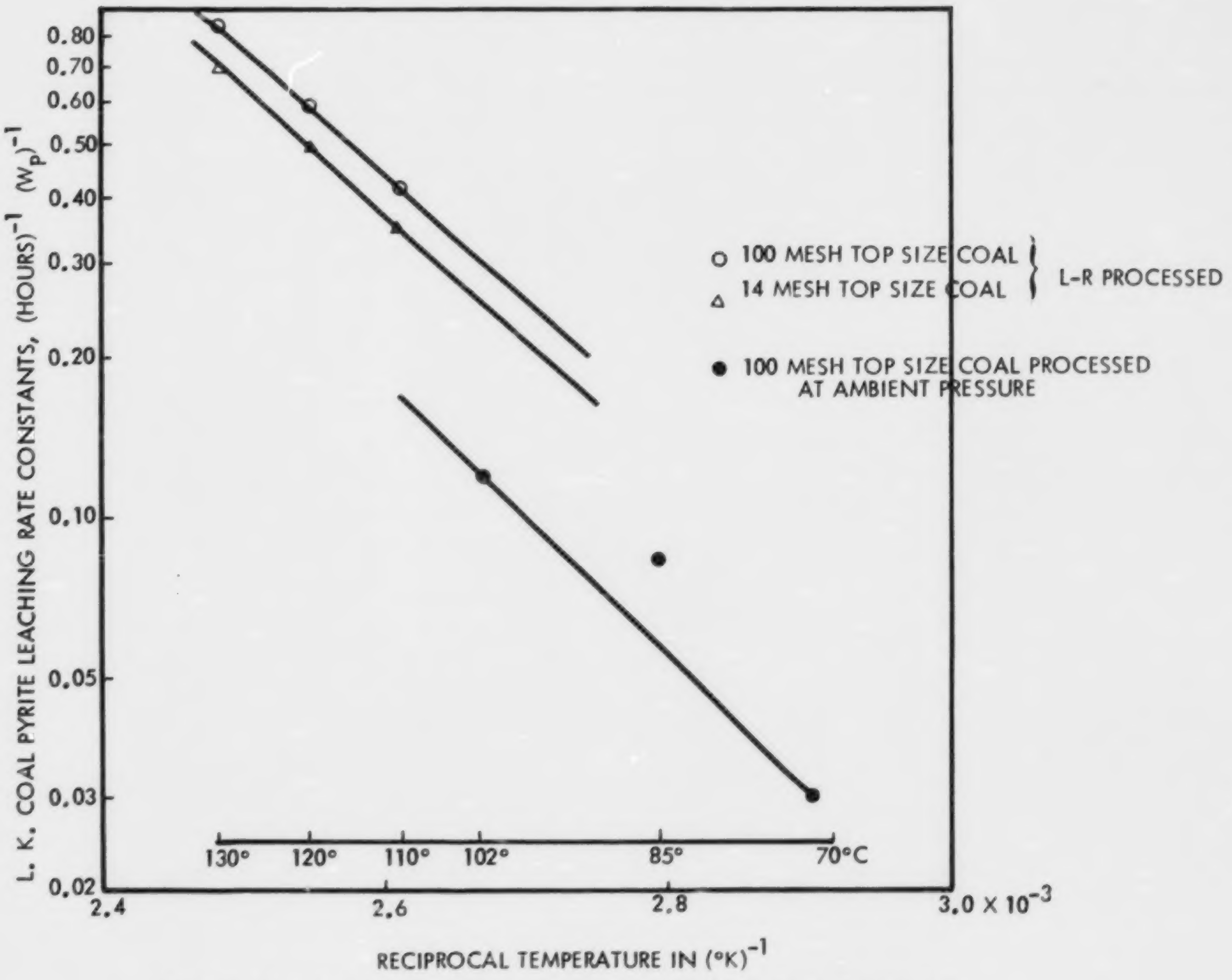


Figure 12. Arrhenius Plots of Pyrite Leaching Rate Constants

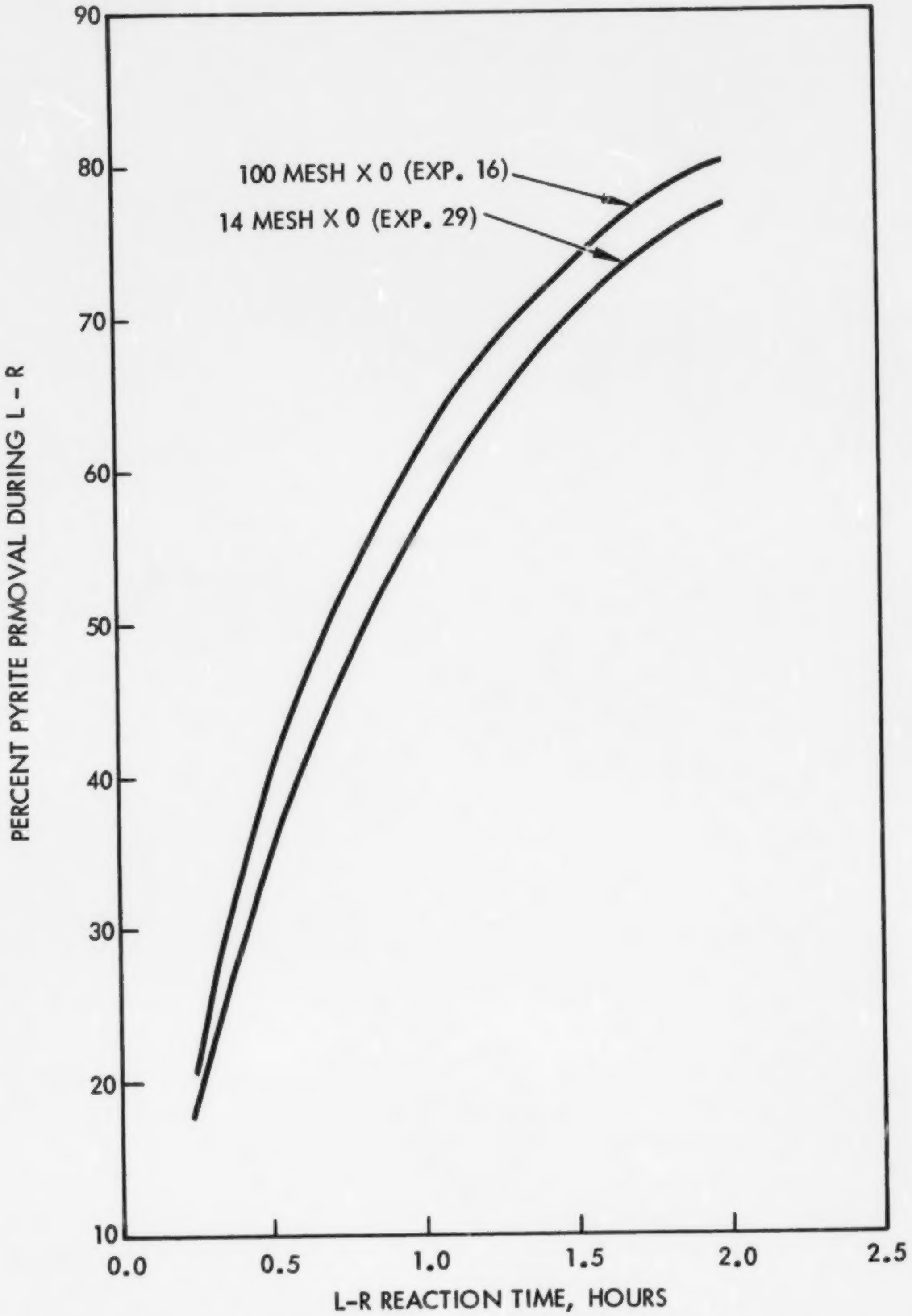


Figure 13. Coal Top Size Effect on L-R Processing of Suspendable L.K. Coal

these data that the coal top size effect on pyrite removal during L-R processing is negligible up to at least the 14 mesh top size. Since in general liquid-solids separation efficiency increases with increase in solids particle size, the data in Figure 13 suggest that desulfurization of L.K. coal should be preferably performed on the 14 mesh top size rather than on finer coal sizes.

2.4.2.5 Slurry Concentration Effects

Slurry concentration, defined as the weight of coal in 100 weights of slurry, does not appear as a variable in either the leaching or the regeneration rates. However, this parameter affects the Y value of the slurry and, therefore, it is an implicit variable of the leaching rate. The higher the coal concentration per unit weight of reagent solution the higher is Fe^{+2} production from pyrite oxidation and therefore the larger the influence on reagent solution Y which is the Fe^{+3}-to-Fe ratio with $Fe^{+3} = Fe\text{-}Fe^{+2}$. Thus, the slurry concentration effect is maximum during ambient pressure, batch coal leaching without reagent exchange (e.g., Mixer and Settler Operations in this program) and zero if coal is processed under constant Y (e.g., continuous, variable rate reagent exchange leaching). During L-R processing this parameter affects also the regeneration rate since an increase in the slurry concentration will result in higher Fe^{+2} concentration in the reagent solution of the slurry which in turn will lead to higher regeneration rates. The magnitude of the effect of slurry concentration on pyrite removal depends on the values of L-R processing parameters which affect the delta between Fe^{+2} production from the leaching reaction and Fe^{+2} consumption in the reagent regeneration reaction.

In Section 2.4.2.3 the slurry concentration effect was discussed in conjunction with the temperature effect on pyrite removal from suspendable L.K. coal during L-R processing. Comparison of the data in Figures 10 and 11 led to the conclusion that in the temperature range of 110° to 130°C it was more efficient to desulfurize L.K. coal as 33 wt. percent slurries than as 20 wt. percent slurries, even though at 110°C the pyrite leaching rate was appreciably lower at the higher slurry concentration (note that twice as much coal is processed per unit time when 33 wt. percent slurries are substituted for 20 wt. percent slurries).

Figure 14 compares data generated from the processing of 33 and 20 wt. percent slurries with all other processing conditions being virtually identical (120°C, 100 psig, 85 psi O_2, 5 wt. percent Fe reagent, 14 mesh top size coals). These data show that at the indicated processing conditions, which represent nearly the center of the range of operational parameters considered feasible for the Meyers Process, the slurry concentration effect on pyrite removal rates is insignificant in the range of 33 to 20 wt. percent slurries. Thus, the data in this Figure suggest that the 33 wt. percent slurry represents the minimum desirable slurry concentration for use in conjunction with the indicated L-R processing conditions.

Review of the entire bank of data in Table D-1, Volume 2 reveals that the slurry concentration effect on pyrite removal rate during the L-R processing of suspendable L.K. coal is principally affected by temperature and oxygen partial pressure. The effect of this parameter increases as the values of either temperature or oxygen partial pressure are reduced within the investigated ranges.

2.4.2.6 Reagent Composition Effects

The Meyers Process reagent is an iron sulfate solution which under certain processing conditions require the addition of sulfuric acid. Thus, its effects on coal pyrite leaching rates should be related to total iron concentration, iron forms (Fe^{+2} and Fe^{+3}) concentrations, sulfate ion concentration, and pH.

The effects of iron forms on leaching and regeneration rates have been discussed in detail in previous sections. It has been repeatedly demonstrated that one of the most important parameters to coal desulfurization by the Meyers Process is the quantity Y, which represents the Fe^{+3}-to-Fe ratio in the reagent solution. The second order dependence of the pyrite

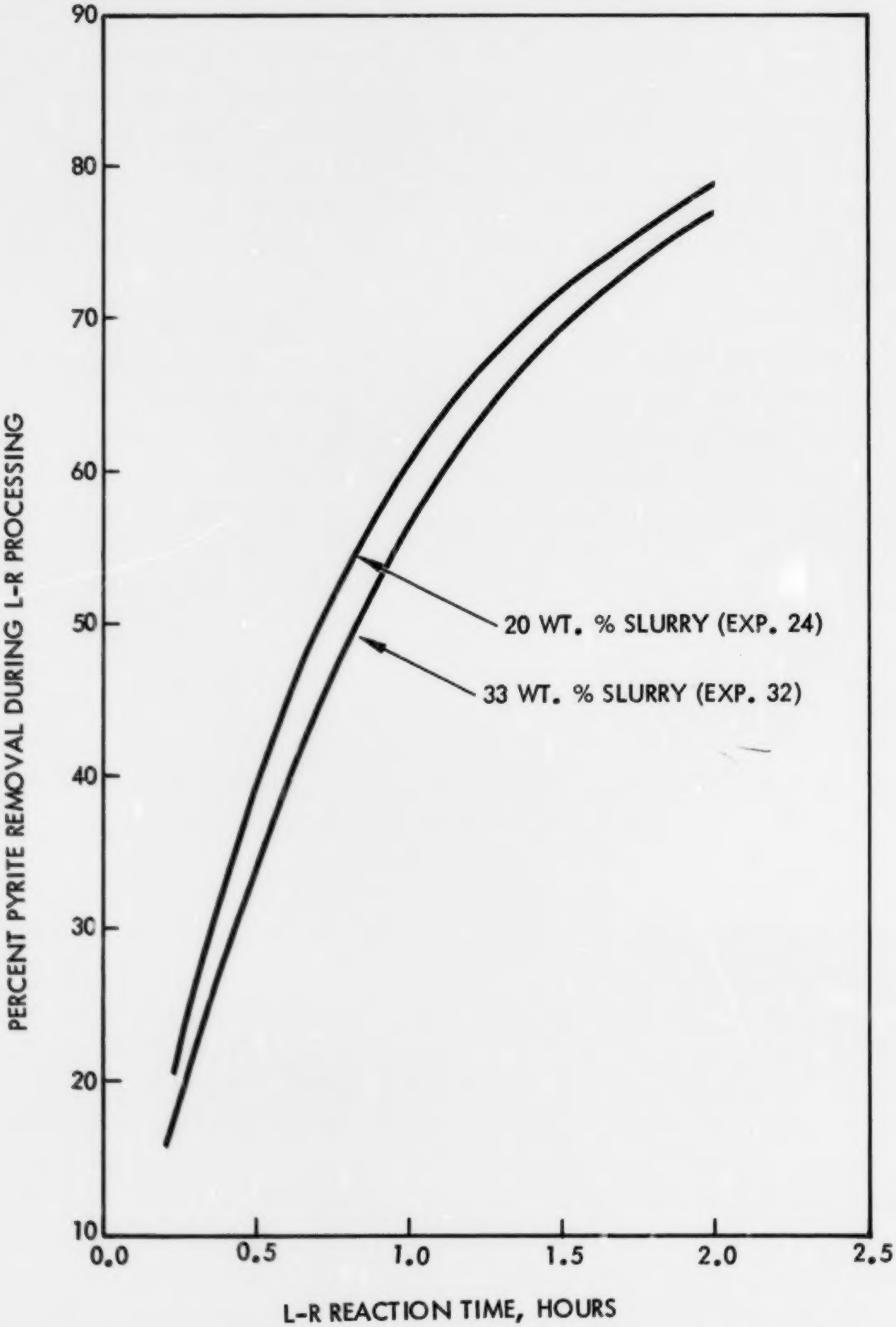


Figure 14. Slurry Concentration Effect on L-R Processing of Suspendable L.K. Coal

leaching rate on this parameter held valid regardless of processing scheme or processing conditions used, provided that the starting reagent contained a soluble iron salt. It was also shown that the regeneration rate exhibits a second order dependence on ferrous ion concentration. Thus, reagent composition in terms of iron forms, especially the ratio of iron forms, has a significant effect on pyrite removal from coal by the Meyers Process.

The sulfate concentration and pH effects of the starting reagent solution on Meyers Process performance were investigated concurrently. Both these parameters were varied through the iron sulfate concentration in the starting reagent and through added sulfuric acid. The sulfate concentration was varied from zero (when the starting reagent was distilled water) to 15 wt. percent (when 5 wt. percent Fe starting reagent of Y = 1 acidified by 2 wt. percent sulfuric acid was used). The corresponding starting reagent pH range was 7 to approximately 0.7. It should be noted, however, that even when the starting pH was 7 its value dropped to below 2 within a few minutes of reaction time because pyrite oxidation generates sulfuric acid. The drop in pH was experienced even under L-R processing where the generated sulfuric acid is, to a large extent, quickly consumed by the regeneration of the ferric ion (oxidation of Fe^{+2}-to-Fe^{+3}).

According to rate Equations (3) through (6) sulfate concentration and pH should not affect directly either the leaching or regeneration rates. The data verified this expectation, except that at L-R reaction times in excess of approximately one hour these two parameters exhibited a small indirect effect on pyrite removal through their influence on the Y of the reagent solution. The data in Appendices A, B, and C show that when L.K. coal was processed under L-R conditions with reagent solutions which did not contain added sulfuric acid, the iron content of the coal during processing did not decrease in proportion to pyrite removed (Experiments 1 through 11, 15, 18 through 22, 41, 42, 43, and 45). Comparison of predicted (Table D-1) and experimental Y values indicated that iron was depositing on the coal at a higher Fe^{+3}-to-Fe^{+2} ratio than that in the reagent solution; thus, the measured Y values in these experiments at t_{L-R}

values in excess of one hour were increasing at lower rates than expected and at longer reaction times the Y actually dropped with increasing t_{L-R} in certain experiments (e.g., Experiment 1). It should be noted, however, that at the t_{L-R} range where iron begins to have an effect on Y, the reagent Y values are high and pyrite leaching is principally limited by the low pyrite concentration in coal; therefore, iron deposition has an insignificant effect on pyrite removal during L-R processing.

The major sulfate concentration-pH effect on the Meyers Process was not on pyrite removal but on sulfate deposition on processed coal and on processed coal washing. The data in Appendices A and B show that, in the experiments where sulfuric acid was not added to the starting reagent, iron and sulfate deposited on the coal during L-R processing when pyrite removal exceeded 40-50 percent and the reagent Y value exceeded approximately 0.5. The deposition of iron and sulfate occurred to approximately the same extent when 3 wt. percent starting Fe reagent solution was used (10.7 wt. percent ferric sulfate) as when 5 wt. percent Fe reagent (17.9 wt. percent ferric sulfate) was used. The same observation is made, with respect to iron deposition, from the data in Appendix C which were generated with reagent solutions whose iron sulfate concentration was derived from coal (iron sulfate was not added to the starting reagent solution); during these experiments sulfate did not deposit on the coal. Iron and sulfate deposition during coal processing under separate leaching regeneration conditions at ambient pressure was minimal ($<$ 0.2 wt. percent sulfate sulfur) even with no added acid to the starting reagent solution and regardless of the iron sulfate concentration in the slurry (up to 10 wt. percent Fe provided the Y was maintained above 0.8).

The above experimental observations are consistent with the Meyers Process chemistry formulated on the basis of elemental sulfur recovery and iron mass balance (ferrous ion production from known quantities of oxidized coal pyrite). According to this chemistry each mole of pyrite is converted to one mole Fe^{+2}, 1.2 moles of sulfate, and 0.8 moles of elemental sulfur through oxidation by Fe^{+3} according to the following reactions:

$$0.4\ FeS_2 + 0.4\ Fe_2(SO_4)_3 \rightarrow 1.2\ FeSO_4 + 0.8S$$

$$0.6\ FeS_2 + 4.2\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 9\ FeSO_4 + 4.8\ H_2SO_4$$

The sum of these two reactions yield the following net reaction for pyrite leaching in the absence of oxygen (separate leaching-regeneration):

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S$$

Thus, each mole of pyrite reacted yields 4.8 moles of sulfuric acid and hence the observed immediate drop in pH. The low pH inhibits the hydrolysis of the iron salts and, therefore, no iron deposition occurs on the coal unless iron sulfate solubilities are exceeded.

Under L-R processing oxygen is added to the process during coal pyrite leaching for the purpose of regenerating the consumed Fe^{+3} (ferric sulfate). Thus, the following reaction takes place simultaneously with the leaching reaction:

$$2\ FeSO_4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

At steady-state, the leaching and regeneration reactions yield the following net reaction:

$$FeS_2 + 2.4\ O_2 \rightarrow 0.6\ FeSO_4 + 0.2\ Fe_2(SO_4)_3 + 0.8S$$

In order to maintain steady-state operation, the product sulfate must be removed continuously from the system at the sulfate-to-iron ratio produced which in molar terms is 1.2. At bench-scale, experimentation was performed in batch mode and the product sulfate was not removed from the system until virtually all the Fe^{+2} in the system was oxidized to Fe^{+3} ($Y > 0.90$). Thus, the 0.6 moles of $FeSO_4$ product per mole of reacted pyrite was virtually all oxidized to the ferric state. In experiments where acid was added to the starting reagent the expected reaction is

$$0.6\ FeSO_4 + 0.3\ H_2SO_4 + 0.15\ O_2 \rightarrow 0.3\ Fe_2(SO_4)_3 + 0.3\ H_2O$$

with the product sulfate remaining soluble. The data in Appendix B, Volume 2 verifies this expectation (acidified runs). In the absence of added acid, the ferrous sulfate oxidation would be expected to yield ferric oxide according to the following reaction

$$0.6\ FeSO_4 + 0.15\ O_2 \rightarrow 0.2\ Fe_2(SO_4)_3 + 0.1\ \underline{Fe_2O_3}$$

with the product iron oxide remaining on the processed coal unless acid washed. The data in Appendix A verifies this expected iron deposition on the processed coal.

The above analysis is totally based on the iron-to-sulfate ratio in the system with no regard to pH. While it adequately explains the iron oxide deposition on the processed coal it does not explain the observed simultaneous sulfate deposition when non-acidified starting reagents were used. One explanation that may be advanced is occlusion of sulfate in the deposited iron. A more probable explanation is the formation of insoluble basic iron sulfate. Chemical analyses on the deposits revealed that the iron-to-sulfate ratio in them was 1.5. According to the literature, the most insoluble form of basic iron sulfate is $3\ Fe_2O_3 \cdot 4\ SO_3 \cdot 9\ H_2O$ which has the same iron-to-sulfur ratio as the deposit on the processed coal. Furthermore, phase diagram data on the iron oxide-sulfate-water system appears to indicate that formation of the above basic iron sulfate could be expected, in small quantities, at the L-R processing conditions utilized in the performed experimentation when the starting reagent did not contain added acid. Addition of sulfuric acid eliminates formation of the basic iron sulfate.

The total iron concentration should also have no direct effect on the Meyers Process according to the formulated rate expressions, Equations (3) through (6), except as it affects Y in operations where neither regeneration nor reagent exchange are operative, e.g., Mixer and Settler Operations. In these operations, the portion of Fe present as Fe^{+3} is being irreversibly reduced to Fe^{+2}. Thus, it is expected that for a given Fe^{+3}-to-Fe^{+2} ratio in the starting reagent solution, the higher the starting Fe concentration in the reagent is per mole of pyrite present, the higher the pyrite removal would be at any reaction time interval. The data in Appendices A through C verify this expectation. For example, pyrite removal in the Mixer Operation from 33 wt. percent coal slurries, after approximately one hour of processing, ranged from 9-12 percent when 5 wt. percent Fe reagent solution was used; 20 wt. percent coal slurries with the same reagent processed for equivalent periods yielded 18-24 percent pyrite removal. Also as expected, the experiments processed with zero iron concentration in the starting reagent led to less than one percent pyrite removal during approximately one hour of Mixer Operation (Appendix C data). The data from the Settler Operation were analogous, but less pronounced and more difficult to distinguish because pyrite removal based on starting coal pyrite was very small in this unit operation and even small noise in the data can easily mask effects on rates or on extent of pyrite removal.

During L-R processing the total iron concentration of the reagent should have no effect on Y, except at the start of the operation if the starting L-R Y is different than 1.0. Since reagent regeneration depends on Fe^{+2} concentration, the higher the Fe^{+2} concentration in the starting L-R reagent solution is, the higher would be the regeneration rate at the start of the operation. Once, however, the Fe^{+2} ions in the starting solution are regenerated, the regeneration rate depends solely on the Fe^{+2} generation rate from the pyrite leaching reaction which does not depend on total iron concentration. For example, a starting 33 wt. percent coal slurry of 5.6 wt. percent Fe reagent with a Y of 0.4 contains 0.6 moles Fe^{+2} per liter; after 15 minutes of L-R reaction, an additional 0.4 moles of Fe^{+2} have been added to each liter of reagent solution from the pyrite leaching reaction and yet, because of regeneration, less than 0.5 Fe^{+2} moles are present in the reagent solution at the end of this reaction interval and only 0.35 moles at the end of 30 minutes reaction time even though approximately 0.7 moles Fe^{+2} were generated by the leaching reaction (see Experiment 32, Table D-1, Volume 2). Thus, it is apparent that the bulk of Fe^{+2} present in the starting reagent was regenerated during the first few minutes of L-R operation. Similar observations are made from the L-R processing of 20 wt. percent slurries in 5 and 3 wt. percent iron reagent; in these experiments the Y of the reagent increases even faster because of the lower pyrite concentration on a per liter of reagent basis.

Equation (5), the regeneration rate expression, and the Y versus t_{L-R} data generated with starting reagent to which no iron was added (Table C-1 Volume 2) indicate that there is an Fe concentration below which its effect on the Y values during L-R processing cease to be insignificant. Yet the data in Figure 15 show that even in the "no added iron" case, where the required Fe^{+3} for the initiation of the pyrite leaching reaction is assumed to have been derived from non-pyritic iron in the coal, the effect of Fe concentration on pyrite removal rates during L-R processing was negligible. It is believed that the explanation is that the concentration of iron in the reagent solution adjacent to the reaction sites is substantially higher than that in the bulk and so is the Y if it is assumed that oxygen diffusion to the vicinity of the reaction sites is faster than iron ion diffusion to the bulk reagent solution. Assuming that this explanation is valid, it is reasonable to assume that the data in Table C-1 could have been predicted by Equation (3) if the Y values near the reaction sites were known.

Pyrite leaching by direct oxidation with oxygen was also considered as an alternate explanation for the unpredictability of pyrite removal rates during the "no added iron" experimentation. However, examination of the data indicated that the reaction product mix was independent of the iron concentration in the feed reagent (see Section 2.4.5.1 page 101). It was, therefore, concluded that a change in reaction mechanism with no apparent change in the process chemistry was very unlikely. It should be noted that the role of iron in Meyers Process chemistry was unequivocally proven from separate leaching-regeneration experimentation.

In conclusion, starting reagent composition did not exhibit any appreciable effect on pyrite removal rates during L-R processing, but it did affect iron deposition on the coal during processing. The latter effect was traced to insufficiency of sulfate ion correctable by the addition of sulfuric acid. For the particular coal processed in this program, the sulfuric acid requirement was estimated at 1.5 percent of the weight of reagent used in 33 wt. percent coal slurries (maximum slurry concentration investigated). Two weight percent sulfuric acid was actually used.

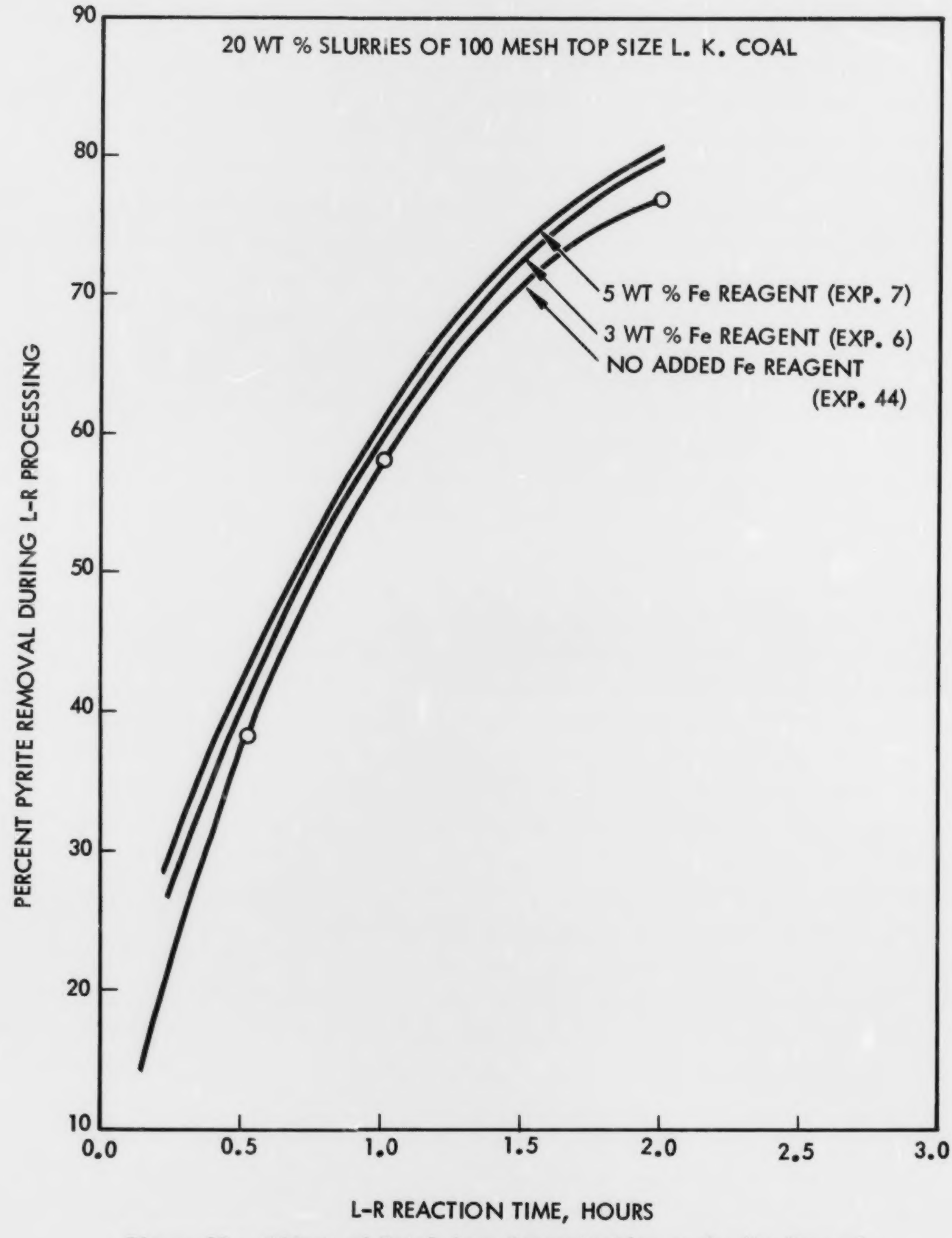


Figure 15. Effect of Total Iron Concentration on Pyrite Removal During L-R Processing of Suspendable L.K. Coals

2.4.2.7 Oxygen Partial Pressure Effects

Figure 16 illustrates the oxygen partial pressure effect on pyrite removal from suspendable L.K. coal during L-R processing with data from Table D-1, Volume 2. Equation (5), the regeneration rate expression, predicts a nearly four-fold increase in regeneration rate when the oxygen partial pressure is increased from 35 psi to 135 psi; the data in Figure 16 show that such an increase in regeneration rate translates to a nearly 70 percent increase in the L-R pyrite leaching rate at 120°C. Thus, the oxygen partial pressure used during L-R processing has an appreciable effect on pyrite leaching from suspendable L.K. coals. It is noted that the experimental data in Appendix B, Volume indicate a substantially reduced effect from that depicted in Figure 16. Analysis of the data revealed that the apparent negligible oxygen partial pressure effect on L-R pyrite removal was due to inconsistent regeneration. Comparison of experimental and predicted L-R Y values indicated that regeneration was efficient throughout the experimentation at 50 psig, but inefficient during the early stages of L-R processing at the higher pressures (refer to Section 2.4.2.2 for details on comparison of predicted and experimental Y values during L-R processing).

2.4.3 Settler Unit Operation

In early program experimentation, approximately one-half of the slurry at the conclusion of L-R processing was transferred to a surge tank where it was permitted to react further at 90°C and ambient pressure while at the same time the settling behavior of the coal was being examined; this practice originated the title of this unit operation. However, laboratory-scale tests on liquid-solids separation of suspendable L.K. coal slurries in 5 wt. percent Fe reagent solution revealed that a settler operation was not necessary even for 20 wt. percent slurries of 100 mesh top size coal. The high pyrite removal rates from 33 wt. percent slurries of 14 mesh top size coal assured that the process did not require a settler. However, the practice of further processing part of the L-R processed slurry in an ambient pressure reactor continued when it became apparent that L-R pyrite leaching rates dropped substantially at pyrite removal levels exceeding 80 percent. The settler now became a stirred, tail-end reactor after the L-R reactor.

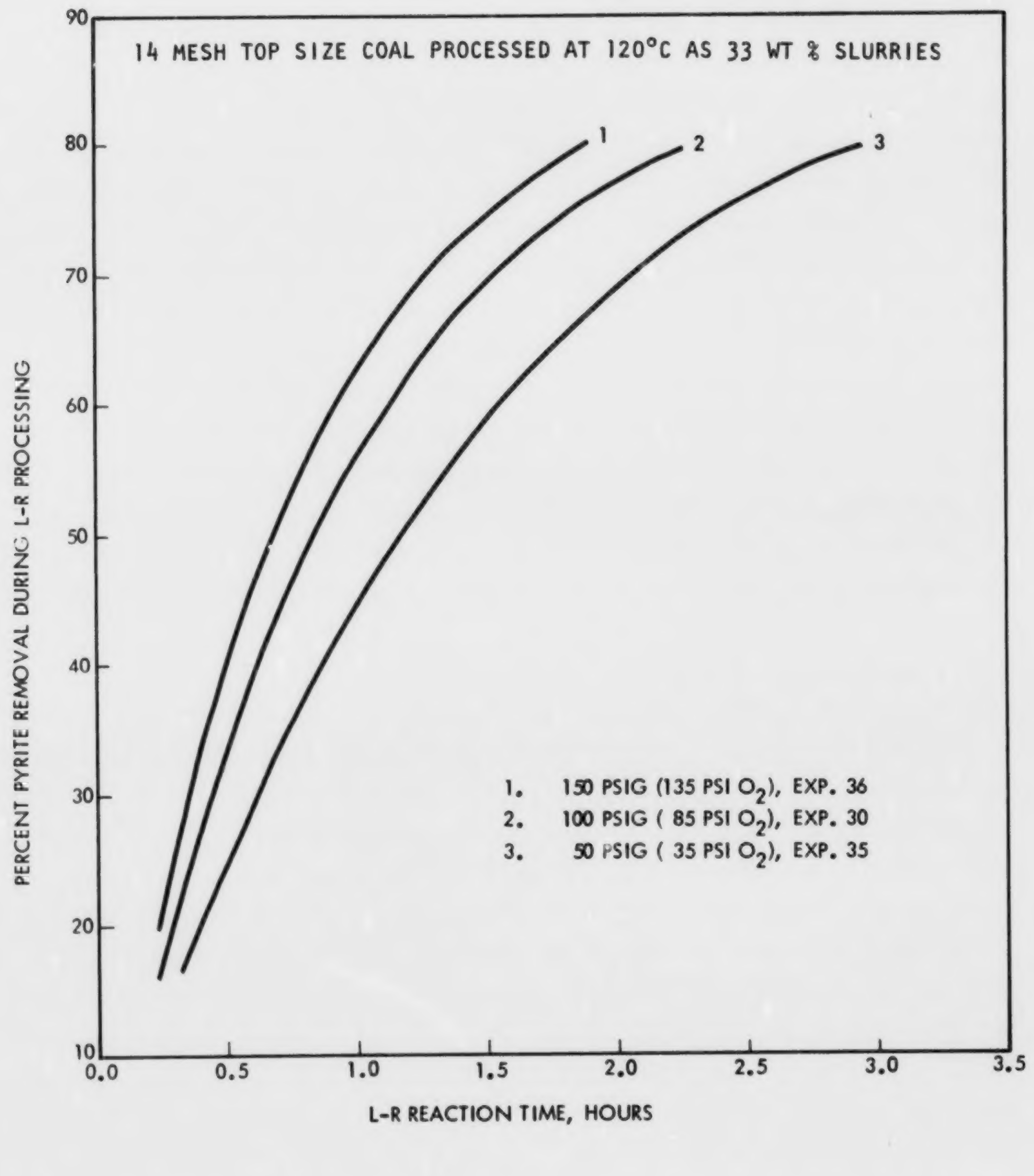


Figure 16. Effect of Oxygen Partial Pressure on L-R Processing of Suspendable L.K. Coal

Settler performance was monitored by sulfur forms analyses of coal samples taken at the start and at the conclusion of the approximately 20 hour operation and by the ferrous ion production during the operation. The percent of the raw coal pyritic sulfur removed during the "settler" operation is easily determined from the rate data listed in Appendices A through C, Volume 2; it is the difference in the S_p removal values listed for "L-R processed coal" and "L-R + settler processed coal". In the majority of experiments pyrite removal in the Settler Operation ranged between 5 and 10 percent of the pyrite in the raw coal or 20 to 40 percent of the pyrite present in the coal at the start of this unit operation. As expected, pyrite removal was nearly zero when the experiment's starting coal slurry was prepared with iron-free reagent (data in Table C-1, Volume 2).

Pyrite removal in the Settler Operation varied because the unit's starting slurry composition varied. Since the reagent was neither exchanged nor regenerated in this unit operation, Meyers Process chemistry dictates that the quantity of pyrite expected to be leached from the coal will be proportional to the quantity of ferric ion present in the reagent of the feed slurry. The rate of removal is governed by Equation (3). Since the operating conditions of this unit (temperature, pressure, reaction time) and the Y value of the feed slurry were very nearly the same in the majority of experiments which included the Settler Operation, the differences in pyrite removal in this operation among these experiments should be principally due to the different values of the reagent Fe to coal pyrite ratio of the feed slurry. The larger this ratio, the higher should be the pyrite removal in the "settler" obtained in the pertinent experiments listed in Appendices A through C, Volume 2. Thus, the less concentrated slurries with the highest Fe content should have yielded the highest pyrite removals after 20 hours of settler processing, and vice versa. The latter expectation is certainly validated by comparing the low iron settler data contained in Appendix C to corresponding data from any of the experiments listed in Appendices A or B. Less extreme comparisons between Experiment 12, Table C-1, which was performed on 20 wt. percent coal slurry, and Experiments 13 through 15, Table C-2, which were performed on 33 wt. percent slurries, validated the above expectations, also. Analyses of the processed coals show that 47 percent of the feed pyrite to the settler was removed in Experiment 12, while the corresponding pyrite removals from Experiments 13, 14, and 15 were 17, 14, and 21 percent, respectively.

In general, the experimental data derived from "settler" processed coal were in qualitative agreement with the predicted behavior based on the chemistry of the Meyers Process and on Equation (3). However, quantitative comparisons were substantially less successful as the data in Table 12 indicate. Table 12 compares percentages of pyrite removal during the Settler Operation computed from (a) sulfur forms analyses of the feed and product coals and (b) the quantity of ferrous ion produced in the "settler", assuming that the chemistry of the Meyers Process applies to this unit operation (10.2 moles Fe^{+2} produced from each mole of pyrite reacted).

TABLE 12. PYRITE REMOVAL IN THE SETTLER OPERATION

Experiment Nos.	23	28	29	30	31	33
% Pyrite Removed Based on						
(a) Coal Analyses	10	14	17	47	13	52
(b) Fe^{+2} Production	32	29	28	32	20	23

Obviously the agreement between the two sets of pyrite removal values is poor, but the difference is equivalent to only 0.1 to 0.2 percent pyritic sulfur in coal which is not too far in excess of expected deviations in the chemical analyses involved. Note that each pyrite removal computation from coal analyses (set (a) in Table 12) required two coal sample analyses for pyrite content, settler feed and settler processed coal samples, each of which contained less than one percent pyritic sulfur with allowable deviation 0.1 percent. On the other hand, Fe^{+2} production was determined from large changes in Fe^{+2} concentration (100 to 200 percent change in Fe^{+2} concentration in the reagent solution, depending on slurry concentration) and, therefore, should yield a more reliable pyrite removal valve. Using equation (3) and a K_L value of 0.07 $(\text{hours})^{-1}$ $(W_p)^{-1}$ for 90°C processing of 14 mesh top size coal, estimated from the Arrhenius plots in Figure 12, predicted "settler" pyrite removal values were computed for the experiments in Table 12. The predicted values ranged from 30 to 36 percent showing relatively good agreement with the pyrite removal values derived from ferrous ion production.

From the above analysis of the "settler" data it can be concluded that the Settler Operation exhibited compliance to the formulated Meyers Process chemistry and obeyed the developed leaching rate expression with rate constant values which are derivable from the ambient pressure A_L and E_L values computed in Section 2.4.1.

2.4.4 Coal Washing Operation

Several processed coal washing schemes were investigated during the early stages of the program in an effort to identify an efficient scheme for washing deposited sulfates from coal processed with reagent which did not contain added sulfuric acid. Multiple stage water washing (3 to 4 stages with water equal to twice the weight of coal per stage), expanded wash times (0.5 to 1.0 hours), and washing with spent reagent did not materially reduce the deposited sulfate. The deposited sulfate could only be removed by agents which simultaneously removed the deposited iron oxide; for example, a single stage coal washing with 1 N sulfuric acid solution followed by two stages of water wash dissolved completely both deposits. This observation combined with Meyers Process Chemistry predictions on iron deposition led to the conclusion that the deposited sulfate was either occluded in or chemically bound with the deposited iron (basic iron sulfate) and, therefore, it could not be removed without the simultaneous dissolution of the iron oxide (see Section 2.4.2.6 for details).

As predicted, the addition of 2 wt. percent sulfuric acid to the starting reagent solution helped to maintain large majority of the process iron and sulfate products in solution and inhibited to a large extent the formation of water insoluble sulfates. Thus, coal processed with acidified reagent required washing principally for the removal of reagent retained by the coal after slurry filtrations; hot water wash accomplished this task effectively as the data (acidified runs) in Appendices A through C, Volume 2 and Table 18 below indicate. However, the problem of sulfate deposition on processed coal was not completely solved with the addition of the 2 wt. percent sulfuric acid to the starting reagent. At long L-R processing reaction times the residual sulfate on processed and washed coal remained unacceptably high (see data in Tables B-1 and B-2, Volume 2). Extrapolation of phase diagram data on the Fe_2O_3-SO_3-H_2O system available in literature appear to indicate that higher sulfuric acid concentrations may be required in the starting reagent than the 2 wt. percent utilized in this program when L-R reaction temperatures exceed 110°C. Efforts to reduce residual sulfate sulfur on processed coal to below 0.2 wt. percent continue. It should be noted that coal leaching with (a) low iron concentration reagent, (b) for less than 3 hours, and (c) at temperatures below 120°C does not present the sulfate deposition problem.

A two-stage wash scheme was adopted as adequate for washing coal processed with acidified reagent (note exceptions in previous paragraph). Each stage consisted of a slurry wash and a cake wash and for each wash a water-to-dry coal weight ratio of 2 was employed. During reagent recycle testing the two-stage wash scheme was preceded by a brief cake wash with a quantity of hot water equal to 50 percent the estimated weight of the dry coal. The collected cake wash filtrate was then used as part of the make-up reagent solution and, thus, reagent recycling was more complete.

Table 13 summarizes Wash Section data derived from the washing of L.K. coals processed under a variety of experimental conditions; the data are typical of the results obtained in this unit operation. The data in the third column of Table 13 represent the estimated quantity of reagent iron on the wet coal after filtration of the L-R or Settler reactor slurries. The quantity of spent reagent retained by the processed coal after filtration was estimated from the difference in weights of the wet filter cake and of the dry product coal plus recovered sulfur residue; the iron was then computed from the measured iron concentration in the filtrate. The fourth column lists the Y value of the spent reagent solution retained by the coal determined from iron analyses on the filtrates. Columns 5 through

TABLE 13. TYPICAL WASH SECTION DATA FROM L-R PROCESSED L.K. COALS

Experiment No.	Coal Top Size (Mesh)	Estimated Reagent Fe on Coal (gm)	Reagent Y	First Stage Wash Filtrates				Second Stage Wash Filtrates				Recovered Fe (Percent)
				Slurry Wash		Cake Wash		Slurry Wash		Cake Wash		
				Fe (gm)	Y	Fe (gm)	Y	Fe (gm)	Y	Fe (gm)	Y	
12 (AG)*	100	15.2	0.85	12.7	0.81	2.8	0.81	0.1	0	0.0	-	102.6
17**	100	21.8	0.84	17.7	0.69	3.5	0.43	0.7	0.03	0.2	0	106.0
25***	14	43.2	0.96	35.4	0.82	7.0	0.80	0.8	0.16	0.3	0.15	100.7
30 (AG)****	14	31.4	0.56	23.0	0.41	4.8	0.42	1.1	0.11	0.4	0.12	93.3

* Coal processed as a 20 wt. percent slurry in 5 wt. percent Fe reagent solution for 5 hours at 120°C and 100 psig; the slurry was also Settler processed.

** Coal processed as a 33 wt. percent slurry in 5 wt. percent Fe reagent solution for 2 hours at 120°C and 50 psig.

*** Coal processed as a 20 wt. percent slurry in 5 wt. percent Fe reagent solution for 6 hours at 120°C and 100 psig.

**** Coal processed as a 33 wt. percent slurry in 5 wt. percent Fe reagent solution for 2 hours at 120°C and 100 psig; the slurry was also Settler processed.

12 show the total iron and the forms of iron (Y value) recovered from each wash. The last column shows the iron recovered in the Wash Section as a percentage of the iron in Column 3.

The data in Table 13 show that better than 95 percent of the reagent iron on the processed coal was recovered in the first wash stage and that the remaining was completely recovered in the second stage; the sulfate recovery values should be analogous. The low Y values in the filtrates of the second stage washes indicate that the iron salt dissolved in this stage was principally in the ferrous state which could mean deposited ferrous sulfate; however, the quantities of iron salt present in these filtrates are insignificant in terms of sulfate deposition of the coal. In fact, the quantity of iron present in the second stage wash filtrates renders the need for a second wash stage questionable.

2.4.5 Elemental Sulfur Recovery Operation

The product elemental sulfur from the experiments listed in Appendices A through C was recovered by leaching the processed and washed coal with toluene. However, special proof-of-principal experimentation was performed on elemental sulfur recovery by hexane and by vaporization in inert gas. The three techniques and the data obtained from them are discussed below in separate sections.

2.4.5.1 Elemental Sulfur Recovery with Toluene

The procedure used to recover the product elemental sulfur during L-R experimentation was described in Section 2.2. In outline, the wet coal from the Wash Section was slurried in twice the estimated dry coal weight toluene, the water on the coal was azeotroped off at 85°C, the toluene slurry was refluxed at 108°C for 30 minutes and filtered hot, and the filtrate evaporated at low temperatures to recover the dry sulfur residue. This procedure constituted a single stage sulfur recovery operation; in the majority of experiments the above procedure was repeated (two stage sulfur recovery).

The sulfur residues from either stage analyzed to between 80 and 90 percent by weight elemental sulfur depending on the attained degree of dryness; a small portion of the residue was carbonaceous material. The weight of residue obtained from the first stage recovery was approximately nine times that recovered from the second stage for virtually every experiment; thus, 90 percent of the recovered elemental sulfur was leached from the coal in the first stage. The quantity of elemental sulfur recovered in each experiment is listed in the sulfur balance section of the mass balance data tables contained in Appendices A through C, Volume 2.

According to Meyers Process chemistry, formulated on the basis of data generated during the ambient pressure leaching of coals with iron salt solutions, coal pyritic sulfur during leaching with iron salts is oxidized to sulfate sulfur (S_s) and elemental sulfur (S_n) at the molar ratio of 1.5. This ratio was computed from the quantity of ferrous ion produced per mole of pyrite removed from coal and from the sulfate sulfur produced in a small number of carefully mass balanced coal extractions with ferric chloride. On the basis of this ratio, 40 percent of the pyritic sulfur removed from the coal should be recovered as elemental sulfur. Actual S_n recovery from these ambient pressure experiments, after 60 minutes reflux of the processed coal in toluene, was between 80 and 90 percent of that expected from the S_s/S_n ratio of 1.5. Conversely, the S_s/S_n ratios derived from the quantities of pyrite removed and elemental sulfur recovered ranged in value from 1.8 to 2.1. This discrepancy in the S_s/S_n values was attributed to incomplete S_n recovery principally due to operational losses rather than leaching inefficiency. In fact, it was concluded that an 80-90 percent recovery of product elemental sulfur represented a reasonable expectation from a bench-scale unit operation which involves a numbers of steps and yields 20 to 40 grams of product from 8 kilograms of slurry.

Simultaneous coal leaching-reagent regeneration does not permit the determination of S_s/S_n ratios from ferrous ion production. Thus, elemental sulfur recovery was used to determine, at least through comparison with ambient pressure data discussed above, the validity of Meyers Process chemistry during L-R processing of L.K. coals. Percent sulfur recovery and the S_s/S_n ratio were computed for each experiment. Percent S_n recovery was computed from Equation (13)

$$\% \; S_n \text{ recovered} = \frac{S_n \text{ recovered}}{0.4 \times S_p \text{ removed}} \times 100 \qquad (13)$$

on the assumption that the S_s/S_n ratio of 1.5 was valid. The S_s/S_n values were computed from Equation (14)

$$S_s/S_n = \frac{S_p \text{ removed} - S_n \text{ recovered}}{S_n \text{ recovered}} \qquad (14)$$

on the assumption that the quantity of recovered S_n represented the entire yield of S_n in the experiment (100 percent S_n recovery). Table 14 summarizes the results.

The data in Table 14 show appreciable scatter, but the range of values is nearly identical to the range of the corresponding values obtained from ambient pressure processed coal (one 30 minute toluene extraction was performed in the first six experiments; therefore, S_n recovery was approximately 10 percent lower than it was in the rest of experiments). The correspondence of ambient pressure and L-R processing S_n recovery data permits at least the inference that the actual S_s/S_n ratio during L-R processing is also 1.5. The data scatter appears to be the same within each group of experiments as it is among groups. Since each group of experiments was performed under different experimental conditions, the 1.5 value of the S_s/S_n ratio evidently applies to the entire spectrum of experimental conditions used in this program. It may be argued that the sulfur recovery from coal processed at 130°C, Experiments 20, 21, 34, and 40, and that from coal processed with iron-free starting reagent, Experiments 42, 44, and 45, points to a higher S_s/S_n ratio than that applicable to the rest of the experiments. At least for Experiments 42 through 45 such conjecture does not appear valid on the basis of sulfate recovery. Because in these experiments the starting reagent solution did not contain iron sulfate, it was possible to estimate the sulfate product of the pyrite leaching reaction; in all four experiments the S_s value pointed to a S_s/S_n ratio of 1.5 (the actual values were 1.7 ± 0.1).

TABLE 14. ELEMENTAL SULFUR PRODUCT RECOVERY FROM THE L-R PROCESSING OF L.K. COAL

100 Mesh Top Size Coal			14 Mesh Top Size Coal		
Exp. Nos.	% S_n Recovered*	(S_s/S_n)**	Exp. Nos.	% S_n Recovered*	(S_s/S_n)**
1	75.9	2.29	23	83.6	1.99
2	77.3	2.23	24	89.2	1.80
3	77.2	2.23	25	85.2	1.93
4	69.8	2.58	26	(71.4)	
5	76.2	2.28	27	86.8	1.88
6	74.5	2.36			
			28	85.8	1.91
7	92.7	1.70	29	84.8	1.94
8	80.7	2.10	30	87.8	1.85
9	89.3	1.80	31	86.8	1.88
10	73.5	2.40	32	73.1	2.42
11	74.4	2.36	33	(60.8)	
12	95.5	1.62			
			34	79.9	2.13
13	90.0	1.78	35	83.0	2.01
14	85.1	1.94			
15	78.9	2.17	36	84.9	1.95
16	88.0	1.84			
			37	71.2	2.51
17	84.5	1.96	38	81.4	2.07
18	85.6	1.92	39	70.2	2.56
19	(65.5)		40	68.1	2.67
20	70.7	2.54	41	43.7	(Coal leaching was performed with defoaming agents)
21	80.1	2.12			
42***	70.0	2.57			
44***	72.4	2.45			
45***	72.0	2.47			

---

* Percent of expected product S_n, the latter computed from the quantity of pyrite removed and $S_s/S_n = 1.5$.

** S_s/S_n value computed from the quantities of pyrite removed and S_n recovered.

*** Coal processed with iron-free starting reagent.

The data in Table 14 proves conclusively that L.K. coal pyrite leaching during L-R processing, at least within the parametric ranges investigated, always yields the two sulfur products specified by the Meyers Process chemistry, sulfate sulfur and elemental sulfur. In addition, these data strongly suggest that the reaction mechanism under all leaching conditions examined to date, including ambient pressure processing, is the same, even though the process may become diffusion limited at some point. This observation lends additional validity to the single rate expression applicability concept already used for describing pyrite leaching rates from suspendable L.K. coal regardless of processing conditions.

Table 14 does not include data from Experiment 43 because toluene leaching was performed subsequent to vacuum drying of the processed coal rendering the recovered S_n value unreliable. The data from Experiment 22 are nearly identical to that derived from Experiment 41 shown in the table. In these two experiments wetting and defoaming additives were used which apparently distorted the sulfur analyses performed on the processed coal rendering meaningful data interpretation impossible; it is believed that the unusually low S_n recovery indicated that the pyrite removal during these experiments was over estimated due to errors in sulfur forms analyses (see also Tables A-7 and B-7, Volume 2). The values in parentheses indicate incomplete recovery of S_n due to traced residue loss, the weight of which could not be accurately determined.

Toluene retention on the product coal was also determined through specially designed experimentation. Approximately 500 grams of dry coal were wetted with 50 percent its weight water and refluxed for 60 minutes in 500 grams of toluene in a well trapped apparatus; the water was azeotroped off prior to reflux. The toluene slurry was then filtered in a closed system and the toluene-wet coal cake was vacuum dried at 100°C overnight in a well trapped oven. A careful mass balance was performed on the coal, water, and toluene from the precise weights of feed and product coal and liquids. The experiment was repeated with twice the weight of feed materials. The mass balances from both experiments were virtually identical and indicated a 0.9 percent increase in the weight of coal, a 0.3 percent increase in the weight of water, and a 2 percent decrease in the weight of toluene. Thus, the total system mass balance shows that 0.9 percent of toluene was not accountable. In terms of coal mass balance, the coal retained 0.9 percent of the toluene; in terms of toluene mass balance it retained 1.8 percent of its weight toluene (note that the water gain represents approximately 0.2 percent toluene). Thus, our estimate of toluene retention on processed coal is one percent of the coal weight.

2.4.5.2 Elemental Sulfur Recovery with Hexane

As a means of reducing process costs, hexane was tried as a substitute to toluene in the recovery of elemental sulfur from processed coal. Leaching experiments were performed with both washed and unwashed, L-R processed, wet coal cakes. The same elemental sulfur extraction procedure was followed as with toluene. However, hexane proved substantially less efficient than toluene in leaching out elemental sulfur from water-wet coal thus, its use was discontinued early in the program.

Wet coal slurried in hexane exhibited the tendency to agglomerate into lumps upon heating; these lumps were difficult to reslurry under normal mechanical stirring, even though they consisted of loosely held coal particles. This observation led to the conclusion that hexane, because of its greater immiscibility with water, enevlops but does not penetrate colonies of wet coal particles suspended in hexane. Eventually, hexane penetrates the coal particles located near the colony boundaries removing the elemental sulfur from them. Thus, its efficiency in removing elemental sulfur from wet coal remains low even under appreciable slurry agitation. To a limited degree hexane's leaching efficiency should depend on extent of slurry agitation since the dimensions of the formed wet-coal colonies appeared to decrease slightly with stirring speed up to a maximum speed at which point centrifugation takes over with the coal being pushed to the sides of the vessel.

Attempts made to improve hexane's sulfur recovery efficiency from wet coals through variations in slurry concentration, degree of agitation, and temperature did not furnish meaningful improvements. The data in Table 15 illustrate the relative S_n leaching efficiencies of hexane and toluene. These data show that only a small percentage of the elemental sulfur in the coal was recovered in the two hexane leaching stages preceding the toluene stage. It is also noted that in three of the four batches of coal less sulfur was recovered in the first stage than in the second; this observation appears to be consistent with the contention that hexane's inefficiency was due to its inability to displace water from coal at reasonable leaching times.

2.4.5.3 Elemental Sulfur Vaporization

Although the atmospheric boiling point of sulfur is 444.6°C, which is somewhat above the decomposition temperature of coal, an appreciable vapor pressure (sufficient for engineering design of equipment for removal of sulfur by vaporization) begins about 250°C (Figure 17). At 350°C (still below the thermal decomposition point of coal), the vapor pressure of sulfur is substantial (∿150 mm Hg). Therefore, it seems reasonable that elemental sulfur could be removed from coal by vaporization either in inert gas stream such as steam or nitrogen or under vacuum, provided that the sulfur does not extensively react with coal during the thermal process.

An initial demonstration of the removal of pyritic sulfur from coal, via ferric ion oxidation, was performed utilizing vaporization for removal of elemental sulfur. In this case, vaporization was effected at 100-120°C and 150 mm of Hg pressure with no detectable coal decomposition or elemental sulfur reaction with coal. In fact, greater than 99 percent pure sulfur was obtained as condensate on a heat-exchanged surface. However, vacuum vaporization in commercial process equipment is thought to be relatively expensive, so that the possibility of vaporizing sulfur from coal at atmospheric pressure and in an inert gas stream was investigated (Table 16).

A coal sample was treated with ferric sulfate under the usual atmospheric leaching conditions but neither water washed to remove iron sulfate from the coal pore structure nor extracted with solvent to remove elemental

TABLE 15. ELEMENTAL SULFUR RECOVERY BY SUCCESSIVE STAGES OF HEXANE-TOLUENE LEACHING

L-R Processed Coal Filter Cakes

Sample A (~1000 Gr. Dry Coal) ↓ Wash — Washed Coal (Wet) — 1/2, 1/2 — 3:1, 4:1 Solvent-To-Coal Extractions

Sample B (~600 Gr. Dry Coal) ↓ Wash — Washed Coal Wet — 1/2, 1/2 — 3:1, 4:1 Solvent-to-Coal Extractions

	Sample A 3:1 Sulfur Out,Gr	Sample A 4:1 Sulfur Out,Gr	Sample B 3:1 Sulfur Out,Gr	Sample B 4:1 Sulfur Out,Gr
1st Hexane	0.74	~0.0	0.29	0.13
2nd Hexane	1.10	0.50	0.31	0.31
Toluene	3.24	3.21	1.38	1.57
TOTAL SULFUR RECOVERED:*	5.08	3.71	1.98	2.01

---

*Estimated overall S_n recovery efficiency >90 percent in all cases.

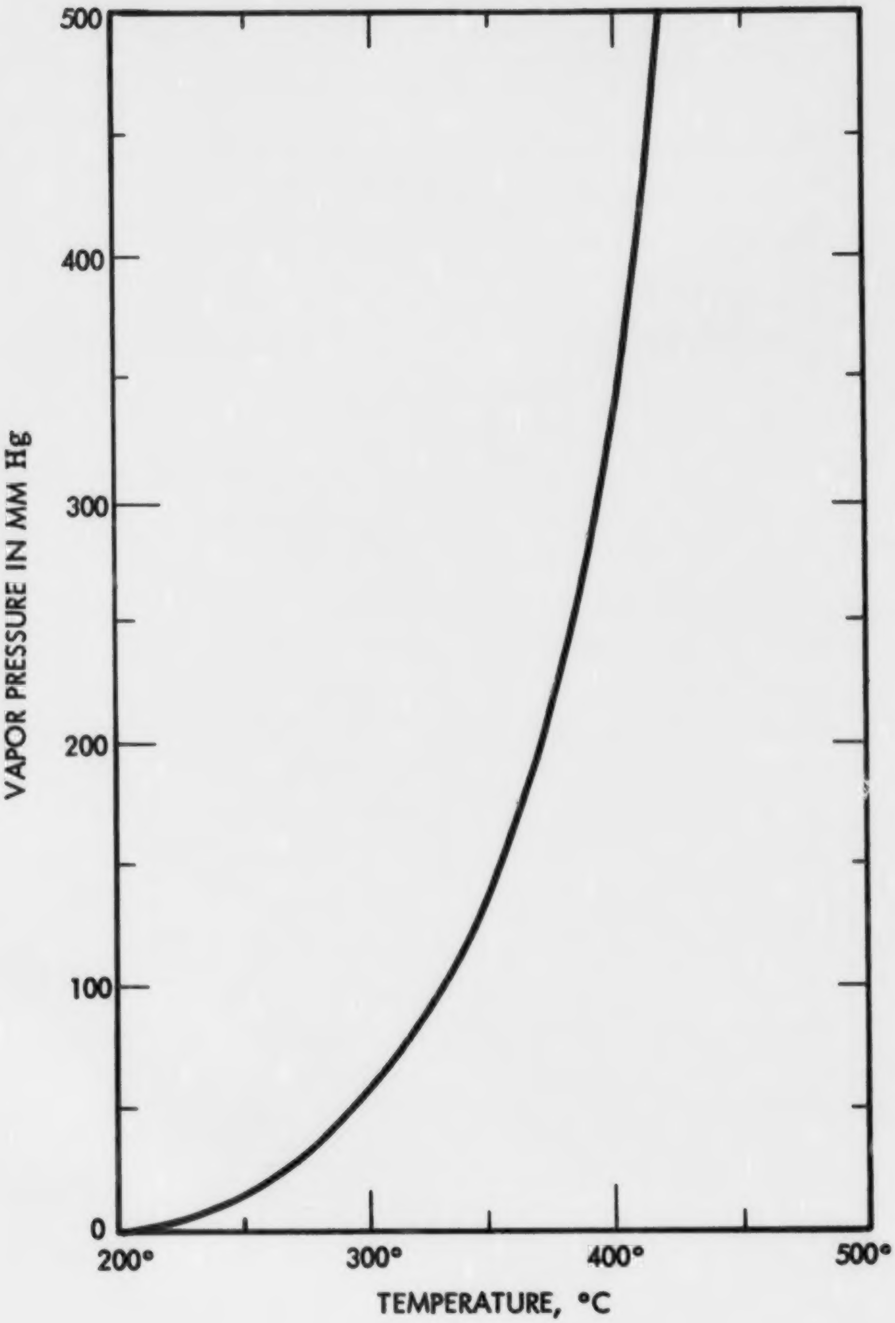


Figure 17. Vapor Pressure of Sulfur

TABLE 16. VAPORIZATION OF ELEMENTAL SULFUR FROM FERRIC SULFATE LEACHED COAL*

Sample No.	Water Washed	Toluene Extracted	Thermal Treatment	% w/w Sulfur		% Weight Loss During Vaporization
				Sulfate	Organic	
1	0	0	0	0.34	1.18	-
2	X	X	0	0.13	0.52	-
3	X	X	220°C/15mm/17 hrs Hg	0.05	0.51	2.7
4	X	0	200°C/3 hrs	0.03	0.92	1.7
5	X	0	250°C/2 hrs	0.01	0.63	1.2
6	X	0	350°C/2 hrs	0.01	0.56	2.8

*200g 100 mesh x 0 Lower Kittanning Seam coal was extracted twice with 2.5ℓ 1N $Fe_2(SO_4)_3$ solution, total residence time 22 hrs. Cursory water wash to remove surface iron sulfate; dried at 110°C under vacuum to remove moisture and as little volatile elemental sulfur as possible. The coal was subsequently split into 10g samples and subjected to the treatment indicated in columns 2 through 4 (X indicates treatment, 0 indicates no treatment). The organic sulfur content of the ROM coal was 0.41 ± 0.04 wt. percent.

sulfur (Sample No. 1). Drying was effected at relatively low temperature in an attempt to remove water but not vaporize large amounts of the elemental sulfur which had been formed. Another sample (No. 2) was washed with water and toluene to remove sulfate and elemental sulfur, respectively. The decrease in "organic" sulfur between samples 1 and 2 (0.66 percent w/w) is a measure of the elemental sulfur which had remained adsorbed on the coal after a cursory drying. Another sample, (No. 3), was further treated under vacuum at 200^{0}C to remove any additional residual sulfur. There was no further decrease in organic sulfur indicating that a maximum of the elemental sulfur had been removed by the toluene extraction; however there was a decrease in the sulfate content.

Temperature Programmed Thermogravimetric Analysis studies show that iron sulfates quantitatively decompose at 450-600^{0}C in an inert atmosphere giving a residue of iron oxide. Apparently, this degradation occurs at somewhat lower temperatures under vacuum and in the presence of a reducing coal environment. Note that the coal weight loss during vacuum treatment was only 2.7 percent of which 0.67 percent could be ascribed to elemental sulfur.

Three samples were contacted with an inert gas stream (argon) in small ceramic boats inserted into a Burrell tube furnace at the specified temperatures and residence times (Nos. 4-6). It can be seen that increasing the temperature of vaporization from 200°C to 350°C increases the quantity of sulfur vaporize. A vaporization temperature of 250-350°C is indicated for use in process design. Note the the weight losses during vaporization did not exceed 2.8 percent (including the loss due to volatilization of sulfur) indicating that sulfur can be relatively selectively vaporized from coal. The method utilized for contacting the coal with the inert gas stream was rather primitive compared to that which can be obtained in commercial size equipment, so that residence times should be substantially reduced.

2.5 SOLID-LIQUID SEPARATION UNIT OPERATIONS

The Meyers Process scheme utilized in the current program involved three solid-liquid separation unit operations: (1) coal separation from spent iron sulfate solutions, (2) coal separation from spent wash water, and (3) coal separation from spent toluene or hexane. All three operations were performed by vacuum filtration with conventional, 4 liter size laboratory apparatuses. The size of the system did not lend itself to quantitative evaluation of parametric effects on these unit operations, nor was there a guarantee that such evaluations would be meaningful to a scaled-up operation using commercial equipment; thus, a systematic study of these unit operations was not undertaken. Qualitatively, filtration efficiency in terms of rates and dryness of the filter cake increased with decreasing liquid density, as expected for constant filter cake depth. Thus, toluene-coal slurries filtered faster than water-coal slurries and the latter appeared to filter faster than spent reagent-coal slurries. Also, while the toluene content of the filter cake was approximately 30 percent of the dry coal weight, the water content of spent reagent and water filter cakes was estimated to be in the 35-40 percent range. The effects of coal top size and slurry concentration in the ranges of 100 to 14 mesh and 33 to 20 wt. percent, respectively, were not easily discernable. It appeared that the 33 wt. percent slurries of 14 mesh top size coal filtered at a higher rate than 20 wt. percent slurries of 100 mesh top size coal, but an effect on filtration rate was not apparent when only one of the above parameters differed. Filtration rates and the moisture content of the filter cake appeared unaffected by variations in L-R processing parameter values.

The feasibility of conducting the described solid-liquid separations on a scaled-up process by commercially available equipment and the type of equipment recommended were determined by outside vendors. Bird Machine Company representatives performed bench-scale tests at the TRW site on actual process slurries and concluded that they can be separated by available commercial equipment at reasonable rates even at solids concentrations as low as 17 percent. They recommended centrifugal separation for the organic solvent coal slurries and either centrifugal separation or rotary drum filtration for the aqueous coal slurries depending on concentration. Details on these evaluations are included in a Bird Machine Company memorandum to TRW reproduced in Appendix F, Volume 2 of this report. Envirotech

Corporation, Salt Lake City, Utah, arrived at similar conclusions using simulated Meyers Process slurries of 100 mesh top size L.K. coal.

2.6 COAL DRYING OPERATION

The toluene-wet coal from the elemental sulfur recovery operation was vacuum dried at 100°C for approximately 16 hours (overnight). This was the only coal drying procedure used in this program. The efficiency of this type of drying operation was determined from the special experimentation performed on processed coal toluene retention described in Section 2.4.5.1.

Selection of drying equipment for the process scheme presented in the process design section of this report was based on information furnished by outside vendors.

2.7 PRINCIPAL CONCLUSIONS FROM BENCH-SCALE DATA

In this report section an attempt is made to summarize the principal conclusions drawn throughout the discussion of the data derived from the L-R processing of suspendable Lower Kittanning coals by the Meyers Process. The emphasis in this summary is placed on information and conclusions vital to the full scale process design presented in Section 5. Of course, the most important information derived from the data generated in this program was the conclusive proof that L-R processing (simultaneous coal leaching-reagent regeneration) of L.K. coals up to at least 14 mesh top size was both feasible and desirable. The expected advantages of L-R processing - combination of two unit operations into one, elimination of the need for solid-liquid separations during leaching, and higher pyrite leaching rates - were attained without any detectable adverse effects on the composition or physical properties of the processed coal. Furthermore, these advantages were augmented by the attained pyrite leaching rates which, under relatively mild temperature and pressure conditions (110°-130°C, 50-150 psig), were higher than expected.

The performed experimentation and resulting data suggested that the L-R processing scheme may be defined by a process train comprised of the following main unit operations connected in series: mixer, L-R reactor, ambient pressure reactor, coal-reagent separation, processed coal wash, coal-water separation, elemental sulfur recovery, and coal drying. The last two unit operations become a single operation when elemental sulfur is recovered by vaporization. Elemental sulfur recovery by organic solvent extraction requires an additional solids-liquid separation operation. Multiple stage processing may be desirable or necessary for certain unit operations (e.g., L-R reactor or coal wash).

In addition to the described process train, the L-R processing scheme requires one or more unit operations in the reagent recycle loop for sulfate and trace element recovery. It is probable that these unit operations would best be employed on process slip streams rather than the entire reagent recycle stream. The generated data were insufficient for the definition of the sulfate recovery unit operations.

In terms of processing function, the identified unit operations may be grouped into four process sections: the reactor section, the wash section, the elemental sulfur recovery section, and the sulfate recovery section. The reactor section - comprised of the mixer, L-R reactor, and ambient pressure reactor - is the core section of the Meyers Process scheme for L-R processing; therefore, it was the most thoroughly investigated of the four process sections.

The three reactors were operated in a batch mode with respect to coal slurry, but oxygen was continuously fed to the L-R reactor. Reactor slurry composition homogeneity was assumed at all times (well-mixed reactors). Coal pyrite leaching took place in all three reactors with the bulk of the pyrite being removed in the L-R reactor, as intended. Throughout the leaching process and regardless of processing conditions coal pyrite was oxidized to sulfate sulfur, S_s, and elemental sulfur, S_n, in accordance with Meyers Process chemistry. The S_s/S_n ratio in the process sulfur product was estimated to be equal to 1.5 regardless of processing conditions.

Pyrite leaching rates in all three unit operations of the reactor section were adequately described by the empirical rate expression

$$r_L = \frac{-dW_p}{dt} = K_L W_p^2 Y^2 \qquad (3)$$

where W_p is the concentration of pyrite in coal at reaction time t in weight percent and Y is the ferric ion-to-total iron ratio in the reagent solution at the same reaction time. The validity of Equation (3) was proven from bulk measurements of Y and W_p during the leaching of both 100 and 14 mesh top size L.K. coals under a variety of processing conditions. Bulk Y measurements were inadequate for use in Equation (3) only when the total iron concentration in the reagent was well below one percent (e.g., in experiments performed with iron-free starting reagent with the process iron being derived from the coal).

In the temperature range investigated, 70° to 130°C, the reaction constant of Equation (3) depended only on temperature and coal particle top size. Between zero and 80 percent pyrite removal the temperature dependence of K_L could be expressed by the Arrhenius-type equation

$$K_L = A_L \exp(-E_L/RT). \qquad (4)$$

Beyond approximately 80 percent pyrite removal the K_L value appeared to be virtually insensitive to temperature change in the range of 102°-130°C; obviously, Equation (4) did not apply to this residual pyrite region. Apparently, a change in the rate occurred when a certain minimum pyrite concentration was reached in the coal. It is believed that this apparent change in mechanism is due to the high ash content of the particular ROM L.K. coal used in this program. Indirect evidence for the validity of this statement is furnished by the coarse coal data in Figure 21, Section 4 of this report, where ROM and cleaned L.K. coal data are compared. These data indicate that a substantial reduction in coarse coal pyrite leaching rate occurred when pyrite removal from the ROM coal samples reached 70 percent, but an equivalent drop in rate was not observed with the cleaned coal. For process design purposes, rate constant values specific to the 80-95 percent pyrite removal region were estimated from the experimental rate data.

For reasons which could not be delineated by the available data, two different A_L values were required in Equation (4) to express the K_L dependence on temperature during mixer processing and L-R processing. Possible explanations are offered in Sections 2.4.2 and 2.4.2.3.

For reagent regeneration during L-R processing, the rate expression developed in the previous bench-scale program with synthetic spent reagent proved valid. The data, however, suggested that the activation energy of the regeneration reaction may be lower for actual spent reagent solution regenerated in the presence of coal than that computed from synthetic spent reagent studies. This apparent catalytic effect could not be quantified from the available data. Qualitative analysis of the data revealed that neglecting this catalytic effect on the regeneration rate would not significantly influence the engineering analysis of the process.

In summary, the empirical rate expressions derived during the current and previous bench-scale programs can be used with confidence for the design of the reactor section for depyritizing suspendable ROM Lower Kittanning coals (higher K_L values may be applicable to cleaned L.K. coals). The following rate expressions and rate constants are applicable to each of the three unit operations:

Mixer:

$$r_L = K_L W_p^2 Y^2 \text{ and } K_L = A_L \exp(-E_L/RT)$$

with $A_L = 3.4 \times 10^5 \text{ (hours)}^{-1} (W_p)^{-1}$ for 100 mesh x 0 L.K. coal

$A_L = 2.7 \times 10^5 \text{ (hours)}^{-1} (W_p)^{-1}$ for 14 mesh x 0 L.K. coal

E_L = 11.1 kilocalories per mole pyrite reacted for both top size coals

The mixer is the unit operation where the coal slurry is prepared and brought to the desired L-R processing conditions (temperature and pressure). Slurry residence time in this unit depends largely on the time required to wet the feed coal. Wetting of Lower Kittanning coals was accomplished by refluxing their freshly mixed slurries for approximately 30 minutes. Thus, slurry residence time in the mixer should be less than one hour.

For a given top size coal, pyrite removal in this unit operation depends on the square of Y and, therefore, on any parameter that affects Y. Since reagent regeneration or exchange does not take place in this unit operation, pyrite removal is highest when the Fe^{+3}-to-pyrite ratio in the slurry is highest (high Fe^{+3} starting reagent concentration, low coal concentration in the slurry). Typical pyrite removal values for L.K. coal were: 20 percent with 20 wt. percent slurries and 5 wt. percent Fe reagent; 10 percent with 33 wt. percent slurries and 5 wt. percent reagent; approximately one percent with slurries prepared from iron-free starting reagent.

L-R Reactor (110°-130°C, 50-150 psig, 14-100 mesh coal top size):

$$r_L = K_L W_p^2 Y^2 \qquad \text{where } Y = 1 - Fe^{+2}/Fe$$

$$r_R = K_R P_{O_2} (Fe^{+2})^2 \quad \text{where } K_R = A_R \exp(-E_R/RT)$$

with $A_R = 6.7 \times 10^5$ liters/mole-atm-minutes

and $E_R = 13.2$ kilocalories per mole of Fe^{+2} oxidized

The above expressions operate simultaneously on the process in the L-R unit operation. The value of K_L to be used in the leaching rate expression depends on temperature and coal top size up to approximately 80 percent pyrite removal, on W_p for a short transition period, and it is probably a pure constant with respect to changes in processing parameters in the 80-95 percent pyrite removal region. Thus,

$$K_L = A_L \exp(-E_L/RT) \text{ for } W_p \geq 1.6 \text{ wt.\%}$$

with A_L (14 mesh) = 7.4×10^5 (Hours)$^{-1}$ (% Pyrite in Coal)$^{-1}$

A_L (100 mesh) = 8.9×10^5 (Hours)$^{-1}$ (% Pyrite in Coal)$^{-1}$

E_L (both top sizes) = 11.1 kilocalories/mole pyrite removed;

also $K_L = (W_p) = W_p - 1.1 \text{ (Hours)}^{-1} \text{ (\% Pyrite)}^{-1}$ for $1.6 \geq W_p \geq 1.2$ wt.%

and $K_L = 0.1 \text{ (Hours)}^{-1} \text{ (\% Pyrite in Coal)}^{-1}$ for $W_p \leq 1.2$ wt.%

Note that the above expressions are strictly valid within the parametric ranges indicated in the parenthesis next to the title of this unit operation. However, there is no reason to believe that they can not be moderately extrapolated.

Ambient Pressure Reactor ("Settler"):

$$r_L = K_L W_p^2 Y^2$$

with $0.10 \geq K_L \geq 0.07 \text{ (Hours)}^{-1} \text{ (\% Pyrite)}^{-1}$ for 90-102°C

The available data did not permit the determination of precise K_L values or the K_L temperature dependence, if any, for temperatures lower than 90°C in this unit operation. The value of 0.07 was estimated from "settler" data generated at 90°C. The 0.10 value is equal to that determined for pyrite leaching from 14 mesh top size L.K. coal at 102°C in the mixer where the reaction appeared to be kinetically controlled, but it is also equal to the estimated value of the diffusion rate K_L determined applicable in the 110°-130°C temperature range after 80-85 percent of pyrite has been removed from coal.

This unit operation serves a dual function: (a) the last few percent of coal pyrite is removed in it and (b) ferrous ion is being generated which can subsequently be used to recover the iron and sulfate products of the process as ferrous sulfate, since ferrous sulfate is less soluble than ferric sulfate.

Figure 18 presents typical process design curves and illustrates the predominance of the L-R unit operation on the overall performance of the Meyers Process. It is noted that under L-R processing, the parametric effects on the individual rates and differences in pyrite removal in the mixer are substantially tempered because of the simultaneous influence of

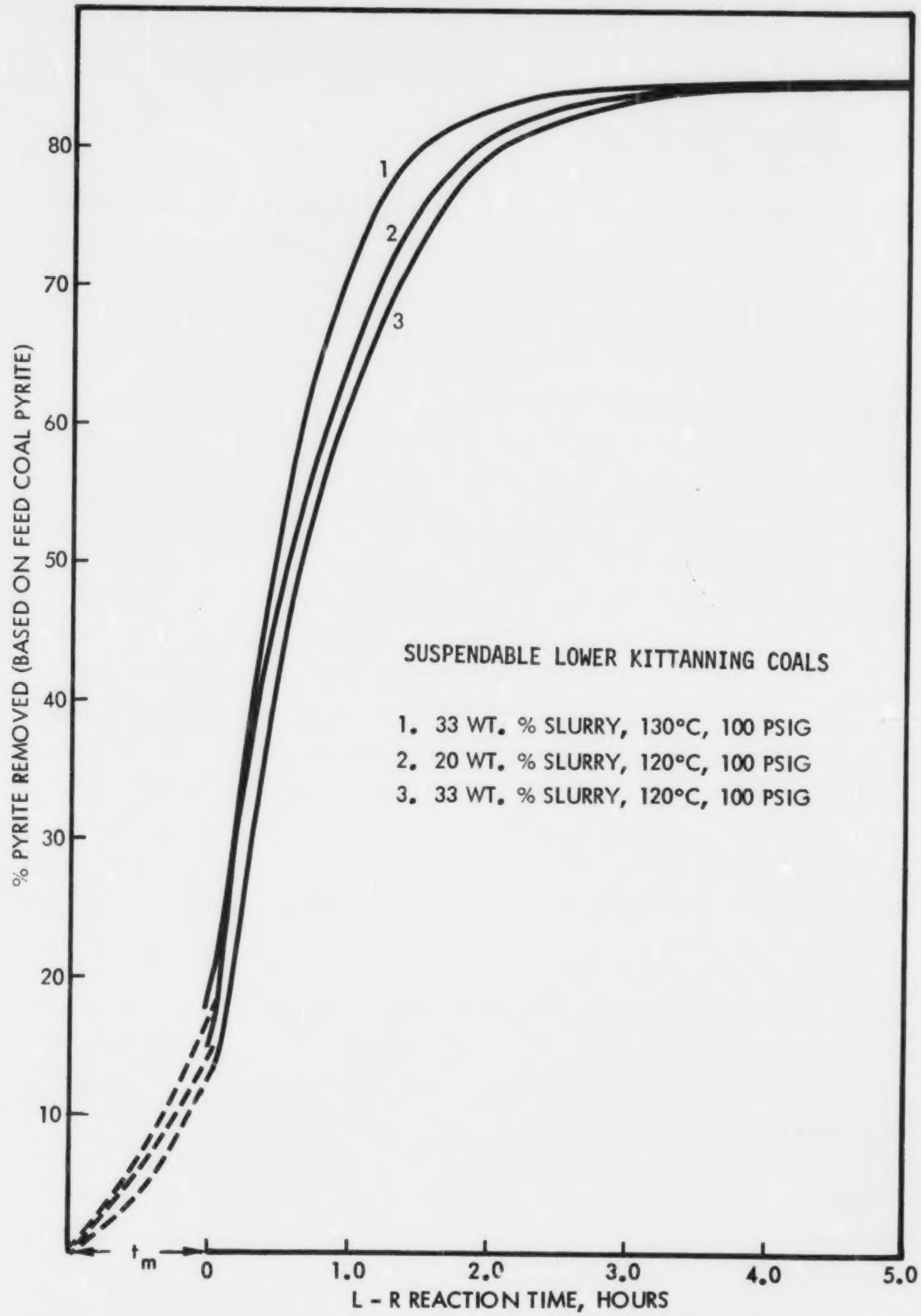


Figure 18. Typical Process Design Curves

the leaching and regeneration rates on process performance in the L-R reactor. Each curve in Figure 18 represents both 14 and 100 mesh top size coals; thus, the coal particle size effect for coal top sizes up to 14 mesh is undetectable under L-R processing. Also, the temperature effect on the leaching rate is less pronounced. Finally, the slurry coal concentration in the 20-33 wt. percent range had virtually no effect on overall process performance even though twice as much coal per unit time was processed when 33 wt. percent slurries were employed as when 20 wt. percent slurries were used. The effect of pressure (oxygen partial pressure) on overall process performance was also small under L-R processing. The apparent process insensitivity to narrow parametric changes, even though individual rates are substantially affected by similar changes in the same parameters, is the result of compensating effects brought about when the individual leaching and regeneration rates operate simultaneously (independent variables become interdependent).

The data in Figure 18 were derived from the rate expressions and rate constant values presented above. For up to 80 percent pyrite removal, data from Appendix D, Volume 2 were used. Appendix D contains similar data for every experiment performed with suspendable coal in the current program. Data in this Appendix are tabulated for up to 90 percent pyrite removal but, at least for the particular L.K. coal used in this program, are only valid up to 80 percent pyrite removal. Note, also, that the data in Appendix D and Figure 18 apply to well mixed reactors only (batch operation).

The Meyers Process design information summarized in this section should only be used with confidence to predict pyrite removal from ROM, run-of-the-mine, Lower Kittanning coals. Limited data on cleaned Lower Kittanning coal (Section 4), Illinois No. 5 coal,[1] and Upper Freeport seam coal appear to indicate that the empirical pyrite leaching rate expression, Equation (3), derived from the study of ROM L.K. coal may also be applicable to these coals provided empirical K_L values are determined for each coal. That the K_L values for different coals could be substantially different is dramatically illustrated in the next section where pyrite removal from L.K. and Upper Freeport coals is compared. It is estimated that the Upper Freeport coal K_L is at least an order of magnitude larger than that of L.K. coal.

2.8 L-R PROCESSING OF UPPER FREEPORT SEAM COAL

A sample of low pyrite ROM Upper Freeport seam coal was available from previously performed screening tests (pyrite leaching under ambient pressure) as part of the Survey Program on the Meyers Process.(1) The coal contained 1.7 wt. percent pyrite (0.9 wt. percent pyritic sulfur) and thus it was considered a good candidate for testing the effectiveness of L-R processing on coal with low pyrite content. Testing of this coal was principally motivated by the substantial reduction in the value of the leaching rate constant observed during the L-R processing of ROM L.K. coal when its pyrite content was reduced by approximately 80 percent to 1.2 wt. percent (the pyrite concentration in the ROM L.K. coal was 7.3 wt. percent).

The available 60 mesh top size ROM Upper Freeport coal was slurried in four times its weight 65°C ferric sulfate solution containing 5 wt. percent iron and immediately processed in the identical manner that L.K. coal was processed. Figure 19 summarizes the data obtained from the L-R processing of Upper Freeport coal. Note that approximately 82 percent of the pyrite in coal was removed during t_m, 1.5 hours slurry residence time in the mixer; at this point the pyritic sulfur content of the coal was only 0.16 wt. percent. An additional 1.5 hours of L-R processing at 120°C increased the overall pyrite removal to 93 percent and reduced the pyritic sulfur content of the coal to 0.07 wt. percent. Obviously, pyrite removal from Upper Freeport coal by the Meyers Process appears to be efficient down to virtually zero pyrite.

In Figure 20 pyrite removal data from nearly identical processing of Upper Freeport and L.K. coals are being compared. It is obvious that pyrite removal from the Upper Freeport coal takes place at higher rates than those for L.K. coal. Since only a single rate experiment was performed with the Upper Freeport coal, it was not possible to determine if pyrite leaching from this coal could be expressed by Equation (3), the empirical leaching rate expression developed from the L.K. investigations, or if a different

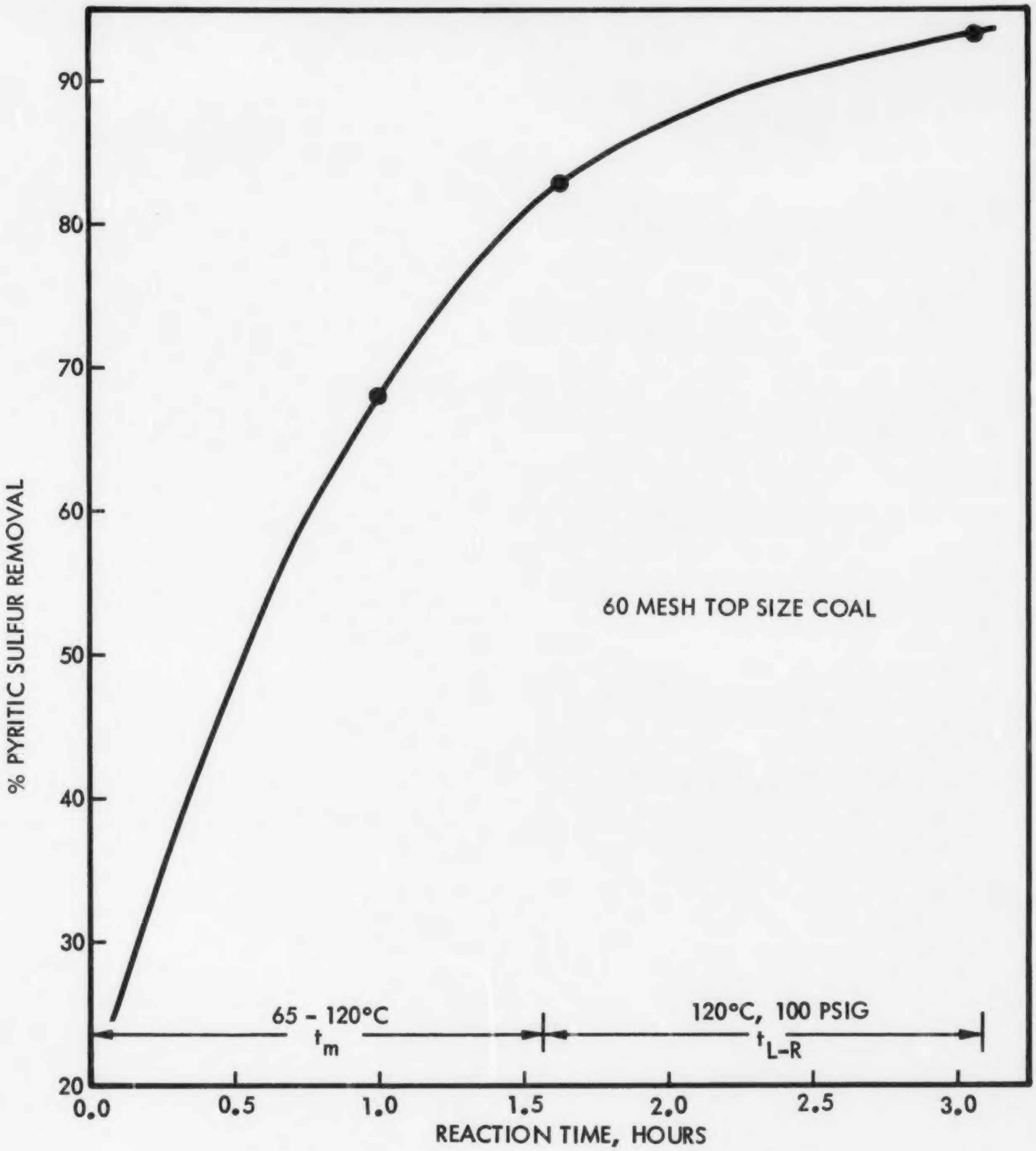


Figure 19. Upper Freeport Coal Leaching with 5 Wt. % Fe Reagent

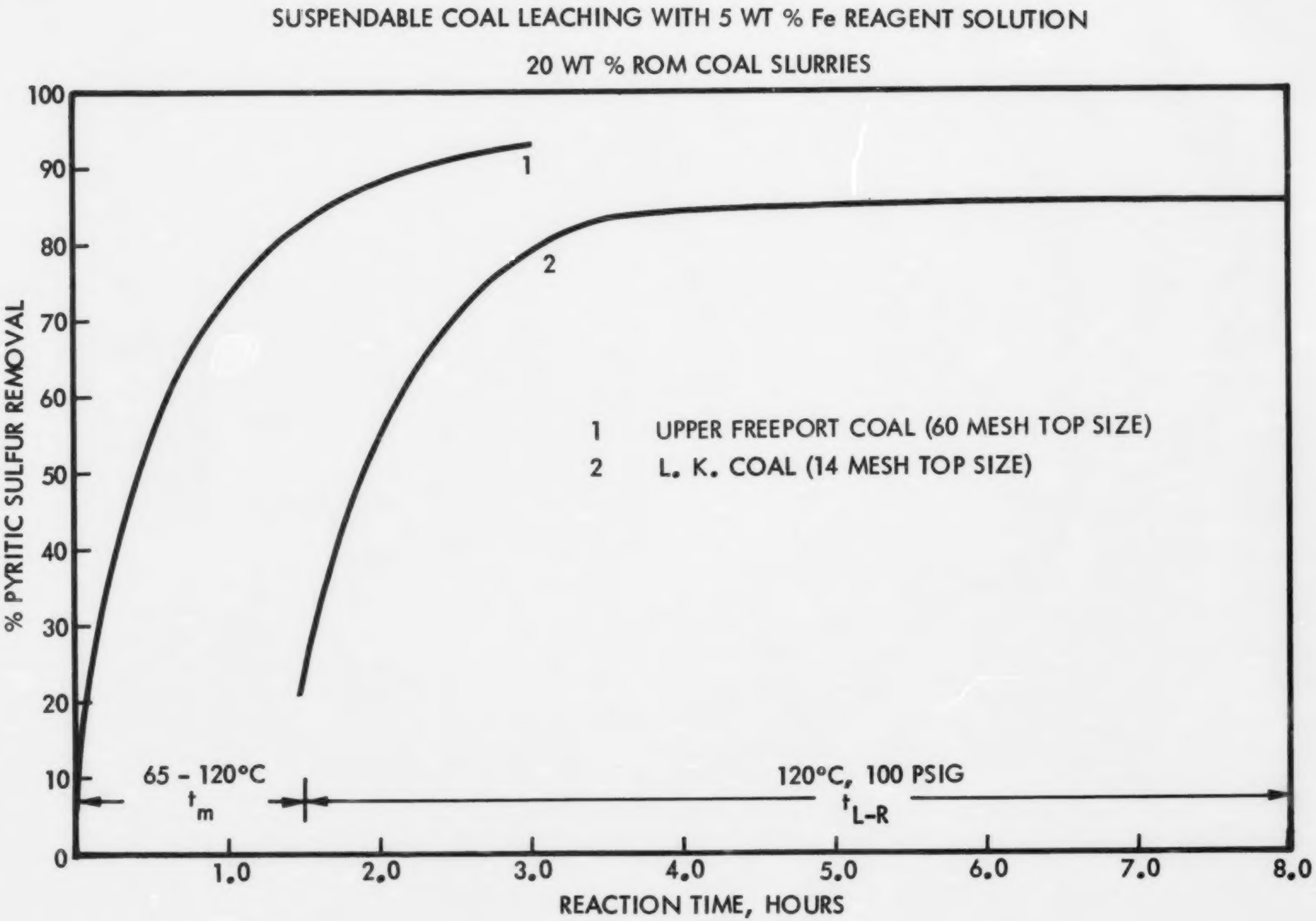


Figure 20. Pyrite Leaching Rates from Upper Freeport and L.K. Mine Coals

expression was required. If, however, it is assumed that Equation (3) applies to Upper Freeport coal, then the data in Figure 20 appear to indicate that the K_L value for the Upper Freeport coal is between one and two orders of magnitude higher than the equivalent K_L value for the L.K. coal.

3. REAGENT RECYCLABILITY-TRACE ELEMENT DATA

A total of 31 L-R experiments were performed utilizing a single batch of recycled reagent. Twenty-nine of these experiments are summarized in Appendices A and B of Volume 2 (Experiments 7 through 11, 13 through 15, 17 through 19,and 23 through 40) and provided for 91 hours of L-R processing exposure under a variety of operating conditions as specified in the Appendices. An additional 10 hours of L-R processing time was accumulated on the recycled solution during special experimentation. Recycled reagent processing exposure over the 101 hours of L-R processing time includes 380 hours of settler processing at 90°C and ambient pressure (for one half of the reagent in nearly all experiments), and 46 hours of mixing and heat-up time prior to L-R processing. Approximately 70 percent of recycled reagent exposure time was accrued subsequent to addition of 2 weight percent H_2SO_4 to the reagent. During the reagent recycle experimention nearly 77 kilograms of dry coal were processed. An average of 18 percent reagent makeup was required to compensate for evaporative losses incurred during processing as well as reagent losses associated with water washing of the leached coal. Aqueous filtrate from the first stage coal wash was utilized in the preparation of make up reagent for the majority of the experiments.

Comparison of the data generated from experiments performed with recycled and fresh reagent indicate no apparent degradation in the activity of the reagent with age or quantity of coal processed, (e.g., compare data from Experiments 23, fresh reagent, and 31, reagent recycled for 40 hours under L-R conditions). A more conclusive proof of the stability of reagent activity during recycling is the fact that the data generated at the beginning and at the end of the reagent recycle experimentation are equally predictable by Equation (3). It is believed that the reagent recyclability tests performed in this program were of sufficient time duration and spanned the range of potential processing conditions of the Meyers Process adequately enough to permit the conclusion that reagent solution recyclability is viable.

Preceding page blank

The reagent recycle investigation also furnished a means of verifying earlier conclusions (Contract No. 68-02-0647)[2] that the Meyers Process removes, in addition to pyrite, non-pyritic mineral matter usually present in coal in minor or trace quantities. This extensive recycling of reagent provided for the build up of trace elements in the reagent and, therefore, furnished the potential of analyzing the reagent for these elements with increased accuracy and of attempting a cursory mass balance of each element in conjunction with coal analyses.

The majority of the elements selected for analysis either have been proven to be hazardous pollutants or are recognized as being potentially hazardous. Included in these categories are As, Be, Cd, Cr, Cu, Li, Mn, Ni, Pb, V and Zn. Other elements were selected because of their corrosion promoting tendencies during processing and/or combustion or because they were previously shown to be amenable to leaching by the Meyers Process.

Analyses were performed on starting and processed samples of both coal and iron sulfate reagent. The detailed description and evaluation of the analytical procedures used can be found in Reference 2. Briefly, all coal and reagent samples were analyzed by atomic absorption (AA) spectroscopy for Be, Ca, Cd, Cr, K, Li, Mg, Mn, Na, Ni, Pb, V and Zn. Arsenic was also determined utilizing a special spectrophotometric procedure. The chloride content of the leach solution was determined using a specially modified silver chloride turbidimetric procedure.

An NBS certified coal (Standard Reference Coal No. 1632) was analyzed concurrently with the selected Lower Kittanning samples as a check on the accuracy of the analytical system. The results are presented in Table 17. A comparison of NBS certified values with analyzed values shows good to excellent agreement for As, Be, Cr, Cu, Mn, Pb, V and Zn as was the case with coals tested earlier and reported in Reference 2.

TABLE 17. TRACE ELEMENT ANALYSIS ACCURACY VERIFICATION
(Concentrations are Shown as ppm in Dry Coal)

	As	Be	Cd	Cr	Ca	Li	Mn	Ni	Pb	V	Zn
NBS Certified Analysis	5.9 ± 0.6	(1.5)	0.19 ± 0.03	20.2 ± 0.5	18 ± 2	-	40 ± 3	15 ± 1	30 ± 9	35 ± 3	37 ± 4
Analysis of NBS Sample in Duplicate:											
	6.1	2	2	16	17	12	33	25	28	24	42*
	5.4	2	4	16	17	13	33	28	24	30	35*

---

*Zinc determination performed on a plasma ashed sample.

Note: Elements in parenthesis are not certified and are for reference only.

One sample of starting coal and one sample of processed Lower Kittanning coal were subjected to duplicate trace element analyses. The processed coal sample was derived from Experiment 31. In this experiment 14 mesh top size coal underwent 3 hours L-R processing at 120°C and 20 hours "settler" processing at 90°C with reagent solution which had already been recycled for approximately 40 hours at 120°C and for nearly 200 hours at 90°C. One starting reagent sample and two recycled reagent samples were also analyzed for trace element content. One of the recycled reagent samples was drawn after 98 hours of L-R processing (87 hours at 120°C and 11 hours at 110°C). The second sample was drawn at the conclusion of the reagent recycle investigations (101 hours L-R processing); it differed from the first by 3 hours L-R processing at 130°C. The second sample was analyzed principally to determine if trace element leaching from coal was enhanced at 130°C. The data from these analyses are summarized in Table 18.

In general, the data in Table 18 show that the decrease in coal trace element concentrations during processing corresponds directly to trace element build up in the recycled iron sulfate leach solution. Elements which apparently are not subject to leaching by the Meyers Process include Be, Cd, K, Li, Na, Pb, and V. Elements appearing to be most susceptible to leaching are As, Ca, Cu, Mn and Zn, with at least 50 percent removal being observed for each. It is also noted that the Cr and Ni concentrations of both coal and reagent solution increased during processing; apparently, this was due to a slight corrosion of the stainless steel apparatus used in these experiments. A similar occurrence is observed with Mg which can not be explained on the basis of available data. It is assumed to be the result of errors in analyses and probably in the analysis of the starting coal which was not performed in duplicate.

An attempt was made at mass balancing the trace elements which exhibited the highest percent removal from coal (As, Cu, Mn, and Zn). The mass balance was performed through the detailed bookkeeping of liquids and solids entering and leaving the process during each experiment performed with recycled reagent. The quantities of trace elements removed from the coal processed in each experiment were computed from the values listed in column 7

TABLE 18. COAL AND REAGENT TRACE AND MINOR ELEMENTS

Element	Trace Element Concentrations in PPM									Estimated Element Removal (Mg/Kg Coal)
	Starting Coal*		Processed Coal*		Starting Reagent	Recycled Reagent (98 hrs. at 110-120°C)		Recycled Reagent (101 hrs. at 110-130°C)		
As	13	16	5	5	1	19	(31)**	19	(27)	10 ± 2
Be	2	2	2	2	0.06	0.9		0.6		0
Ca	1590	-	7.6	7.6	5	318		293		1582 ± 159
Cd	3	1	1	1	0.07	0.14		0.14		1 ± 0.3
Cl	NA	NA	NA	NA	37	175		110		ND
Cr	39	36	55	59	6	30		30		ND
Cu	27	27	7	7	0.09	64	(66)	58	(57)	20 ± 3
K	4030	-	3170	3160	0.6	1.0		0.7		865 ± 360
Li	37	37	42	37	NA	NA		NA		0
Mg	946	-	4171	4414	6	238		224		ND
Mn	26	25	8	8	28	30	(88)	32	(76)	18 ± 3
Na	637	-	734	753	4	36		20		0
Ni	48	43	50	50	6	154		136		ND
Pb	17	18	22	25	0.44	0.65		0.58		0
V	55	50	50	55	NA	NA		NA		0
Zn	30	26	13	14	0.78	52	(46)	52	(40)	14 ± 4

* Duplicate analysis performed for most elements.

** Values in parentheses represent the expected trace element concentrations in the reagent based on coal analyses and on the quantity of coal processed with the same batch of reagent (adjusted for make-up).

NA - Not analyzed.

ND - Not determinable from available data.

of Table 18. In turn, these values were computed from the analyses performed on the starting coal and the processed coal from Experiment 31 (columns 2 and 3, Table 18). The assumption was made that the quantity of trace element removal per unit weight of coal processed was the same for all experiments and equal to that determined for Experiment 31; that is, L-R reaction time beyond one hour of processing and changes in slurry concentration, pressure, and temperature had no effect on trace element removal (note, however, that only a limited number of experiments were performed at temperatures, pressures, and slurry concentrations different from those of Experiment 31). The trace element bookkeeping process began with the batch of pure reagent solution used as the feed to the reagent recycle tests and ended 30 experiments later when the reagent recycle investigations were completed. Trace element build up in the reagent during each experiment was computed by adding to the known reagent composition at the start of the experiment the quantity of trace elements leached from the coal during the experiment; the new reagent solution composition was appropriately adjusted for trace element and liquid removals (losses) during transfers and coal wash and for additions through reagent make up.

As a result of the above bookkeeping operation, it was possible to compute the expected concentration of the selected trace elements in the reagent solution as a function of reagent recycle time. In Table 18, computed trace element concentrations (values in parentheses, columns 5 and 6) are compared with the corresponding trace element concentrations obtained from direct trace element analyses of the recycled reagent solutions. Reasonably good agreement is seen for As, Cu, and Zn, but not for Mn. The reason for the discrepancy between computed and analyzed Mn concentrations could not be discerned from the available data; it is believed to be due to the analyzed high Mn concentration in the starting reagent solution which, if erroneously high as believed to be, would make the computed concentrations higher than should actually be. The agreement between computed and analyzed trace element concentrations for three out of four mass balanced trace elements adds substantial credence to the values in column 7 of Table 18. These latter values are not only important to the design of a product recovery system for the Meyers Process, but also to the evaluation of the environmental benefits derived from the utilization of the Meyers Process for the desulfurization of a particular coal.

Comparison of the data in columns 5 and 6, Table 18, appears to indicate that there was no significant increase in the leaching of trace elements when L-R processing temperature was increased from 120°C to 130°C. Both, the analyzed and computed trace element concentrations lead to the same conclusion.

Calcium, one of the minor elements in coal, was also substantially leached from coal during processing. Because of the high quantity of calcium leached from the coal, relative to trace elements, and because of its low solubility in the reagent, this element was periodically removed from the recycling reagent solution as a precipitate. Approximately one gram of white crystalline precipitate was recovered from the reagent solution per kilogram of coal processed. Emission spectrographic analyses of six precipitates revealed that Ca was the only cation present in the precipitates in larger than trace quantities. The anion of the precipitates was not determined, but in all probability it was sulfate. One precipitate was analyzed in duplicate for trace cation content; the data are presented in Table 19.

TABLE 19. TRACE CATION CONTENT OF CALCIUM PRECIPITATES RECOVERED FROM SPENT REAGENT

Sample	Trace Cations Present in the Calcium Precipitate, ppm													
	As	Be	Cd	Cr	Cu	Li	Mg	Mn	Ni	Pd	Si	Sr	V	Zn
A	<1	<0.5	5	10	8	<1	5	12	67	7	10	50	<1	9
B*	<1	<0.5	8	14	6	<1	5	12	67	<1	10	30	<1	<0.2

*Sample B is a duplicate of A

Attempts to mass balance Ca using the procedure followed for trace element mass balancing described earlier were not very successful. Less than 25 percent of the Ca removed from coal, estimated from before and after processing coal analyses, could be accounted for by the recovered precipitates (assumed to be $CaSO_4 \cdot 2H_2O$) and by the build up of dissolved Ca in the reagent solution. This was not completely unexpected since a small amount of precipitate could have deposited on the coal during processing and have been leached out and not recovered during coal wash (note that the quantities involved are 3-4 grams of precipitate per kilogram of coal subjected to washing).

4. PROCESSING OF COARSE COAL

Coarse coal can easily be separated from the leaching solution thus L-R processing (simultaneous coal leaching-reagent regeneration) is not necessarily advantageous to coarse coal unless it improves substantially depyritization rates over those obtained during ambient pressure processing. The substantial increases of pyritic sulfur leaching rates with increasing temperature observed with suspendable coal slurries suggested that coarse coal pyrite removal rates may indeed improve substantially under L-R processing. However, a brief experimentation with 3/8 inch x 0 L.K. coal revealed that L-R processing of coarse coal results in only marginal gains in rate over those attainable at 102°C under ambient pressure processing (separate leaching-regeneration) as the data in Section 4.1 indicate.

In general, L-R processing of coarse coal was similar to that described for suspendable coal. The major difference being that coarse coal was processed as a semi-fluidized bed while suspendable coal was processed as a well mixed, partially circulating slurry. In order to accommodate this difference, the existing suspendable coal processing reactor was modified by the addition of a reinforced wire mesh basket and lid to support and confine the coal during reagent circulation. Two additional thermocouples were installed to monitor internal coal bed temperatures. The coal bed density was approximately 0.7 kg/liter. Also, the reagent circulation rate was decreased to 3 liters per minute (as determined by indirect measurement). Procedural changes were as follows: (1) slurry was charged into the reactor through the reactor top flange opening, (2) only reagent composition was monitored during L-R processing since the circulated reagent contained less than 1.5 percent solids (these solids being non-representative of the whole coal), and (3) reactor drainage consisted of reagent removal through the reactor bottom while the retaining basket and coal were removed through the reactor top.

All additional processing (water washing, elemental sulfur extraction and coal drying) was carried out in a manner identical to that employed during suspendable coal processing.

A major difficulty encountered during coarse coal processing was maintenance of uniform reagent flow throughout the coal bed. To ensure uniform flow, the retaining basket sides were removed so that coal-reactor wall contact prevented channeling around the basket. Additionally, process coal weights were reduced from the planned 4 to 5 Kg range to a 1.5 to 3 Kg range. Verification of uniform flow was made by positioning thermocouples within the coal bed and evaluating their response to temperature changes in the circulating reagent (slow response was taken to indicate regions of low flow).

4.1 L-R PROCESSING DATA FOR COARSE COAL

Three coarse coal leaching experiments were performed under processing conditions using acidified reagent. These consisted of two experiments of 8 hours each and a single experiment of 2 hours. Settler processing was not employed during any of these experiments. One 8 hour experiment (Experiment 46) consisted of processing approximately 3200 grams of coal using 2 weights of reagent per weight of coal while the other (Experiment 47) consisted of processing nearly 1900 grams of coal using 4 weights of reagent per weight of coal. In the 2 hour experiment (Experiment 48), approximately 1700 grams of coal were processed using 4 weights of reagent per weight of coal. Processed coal analyses for these experiments are presented in Table 20. The analyses are seen to be internally consistent, although Experiment 46 results seem to indicate slight iron oxide deposition (probably due to slightly inadaquate reagent acidification).

All three experiments resulted in rather low pyrite removals. Pyrite removals during mixing (t_m), calculated on the basis of ferrous iron production, were 6, 15 and 14 percent for Experiments 46, 47 and 48, respectively. The low percentage pyritic sulfur removal observed during t_m in Experiment 46 was due to a low starting reagent Y value (0.65) and the high coal-to-reagent ratio used in this experiment (0.5); the other two experiments were performed at a coal-to-reagent ratio of 0.25 and at starting Ys >0.9.

TABLE 20. L-R PROCESSING OF 3/8 INCH x 0 L.K. COAL IN 5 WT. % FE REAGENT* AT 120°C AND 100 PSIG (85 PSI O_2)

Experiment No.	Coal Composition Wt. % (Except Heat Content), Dry							% S_p Removal	
	Ash	Heat Content Btu/Lb	Total Sulfur S_t	Pyritic Sulfur S_p	Sulfate Sulfur S_s	Organic Sulfur S_o	Iron, Fe	Based on Analyzed S_p	Based on Corrected S_p
Starting Coal	28.91 ± .52	10,448 ± 106	4.28 ±.14	3.56 ±.18	0.35 ±.03	0.37 ±.03	3.68 ±.13		
46	31.16	10,246	2.86	2.11	0.25	0.50	3.21	41	37
47	29.40	10,638	2.82	2.27	0.22	0.33	2.67	36	38
48	30.27	10,465	3.16	2.50	0.14	0.52	2.84	30	26

* The reagent was acidified with 2 Wt. % H_2SO_4.

Comparable 102°C data for 3/8 inch x 0 L.K. coal are not available.[1] However, 102°C data are available for the 1/4 inch x 0 L.K. coal used in the previous bench-scale program. These data are presented in Table 21. This 1/4 inch x 0 L.K. coal had a starting pyritic sulfur content of 3.48 percent and attained 13 percent pyrite removal during mixing and heat up. High reagent Y values were maintained by frequent reagent exchange.

TABLE 21. PYRITIC SULFUR REMOVAL FROM 1/4 INCH x 0 L.K. COAL AT 102°C

Process Time (hrs)	Average Y Value	Pyrite Removal, Percent
2	∿0.8	32
4	∿0.9	46
6	∿0.9	55
8	∿0.9	62
10	∿0.9	65

A comparison of the 3/8 inch x 0 L.K. coal data with the 1/4 inch x 0 L.K. coal data indicates that the average pyritic sulfur removal rate during the first 2 hours of processing was slightly lower for the 3/8 inch x 0 coal than for the 1/4 inch x 0 coal. Average reagent Y values were approximately equal for both experiments during this time. Between 2 and 8 hours of processing, however, the average pyritic sulfur removal rates are seen to be substantially higher for the 1/4 inch x 0 L.K. coal (102°C processing) than for the 3/8 inch x 0 L.K. coal (120°C processing) despite the lower pyrite content of the 1/4 inch x 0 coal (reagent Y values being nearly equal for both experiments during this time). Thus, the pyrite leaching rate constant of 3/8 inch x 0 L.K. coal is lower at 120°C than the rate constant of 1/4 inch x 0 L.K. coal at 102°C. This seems to indicate that pyrite removal rates quickly become diffusion limited during processing of coarse coals.

While the benefits of elevated temperature processing of run-of-mine coarse coal appear to be minimal, it will be shown in the following sections that 102°C processing data indicate potential for application of the L-R processing mode to specific coarse coal size fractions.

4.2 CLEAN COAL GRAVITY FRACTION PROCESSING

The relative rates of desulfurization of run-of-mine fine L.K. coal (100 x 0 mesh) and coarse L.K. coal (1/4 inch x 0) are compared in Figure 21 along with the pyrite removal rate curves of narrow size cuts of clean and run-of-mine coarse L.K. coal, illustrating the enhancement of rate effected by cleaning coal. These data on coarse coal were generated with 100-500 grams 1/4 inch x 0 Lower Kittanning coal (or size fractions therefrom) slurried in iron sulfate solution (5 wt. % Fe, 15-20 wt. % solids). The ROM 8 x 14 mesh coal fraction is seen to have lower pyrite removal than 1/4 inch x 0 coal for all times prior to 40 hours leaching, at which time both their pyrite contents and pyrite removal rates are seen to become nearly equal. Upon cleaning the 8 x 14 mesh size fraction (float-sink removal of 20 percent of the total coal), however, its pyrite removal rate closely approximates that of 1/4 inch x 0 coal during the first 9 hours of processing. After the initial 9 hours of processing, pyrite removal rates of the cleaned 8 x 14 mesh coal are seen to approach that of a much finer mesh coal. Coal analyses from these experiments are presented in Table 22. The results show that: (1) clean coal reacts substantially faster than ROM (raw) coal, (2) coarse coal (in this case, a cleaned narrow size fraction) can be desulfurized to near zero pyrite (0.09 percent pyritic sulfur), and (3) the desulfurized clean coal has 0.92 percent total sulfur at a 14736 Btu/lb heat content, which is very close to the Federal Standards for New Stationary Sources (0.89 percent sulfur at this heat content).

TABLE 22. CHEMICAL REMOVAL OF PYRITIC SULFUR FROM CLEANED 8 x 14 MESH LOWER KITTANNING COAL AT 102°C

	% W/W SULFUR					
Coal	Total	Pyritic	Sulfate	Organic	Ash	BTU
Whole Coal	4.43	3.37	0.43	0.68	20.11	12066
Sink (1.75) (20.4%)	13.7	12.4	1.22	0.04	71.6	-----
Float (1.75) (79.6%)	2.02	1.06	0.23	0.73	6.92	13899
Float - 48 hr leach	0.92	0.09	0.03	0.80	5.38	14736
Whole - 48 hr leach	1.39	0.57	0.04	0.78	14.88	13257

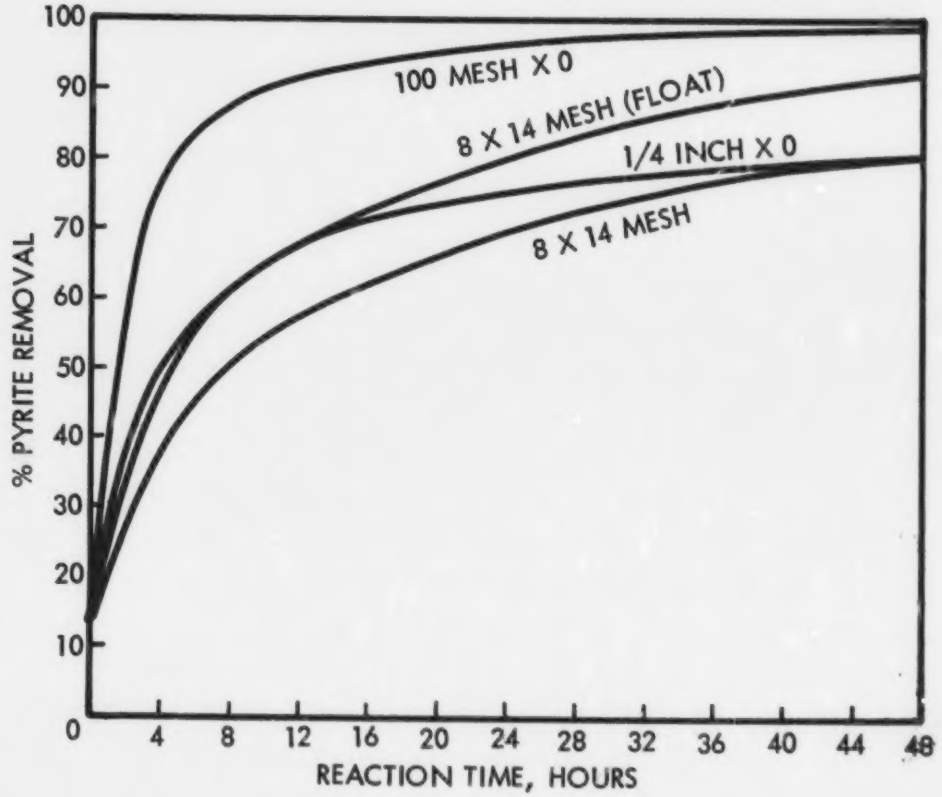


Figure 21. Pyritic Sulfur Removal from ROM and Cleaned L.K. Coal at 102°C

4.3 PRELIMINARY DATA ON COARSE COAL PROCESSING BY SIZE FRACTION

Typical S_p removal values from 1/4 inch x 0 coal are presented in Table 23 along with the ratio of the effective leaching rate constants measured for -100 mesh and 1/4 inch x 0 Lower Kittanning coal with identical reagent Y and coal pyrite values. It is interesting to note that this ratio does not remain constant with extent of pyrite removal; thus, the leaching rate constants of various top sizes of the same coal cannot be related by a single proportionality constant. This observation can be attributed to the fact that a given top size coal is comprised of a wide range of coal particle sizes with each particle size being associated with a different pyrite leaching rate constant.

TABLE 23. PYRITE LEACHING OF 1/4 INCH x 0 LOWER KITTANNING COAL AT 102°C

Reaction Time, Hours	Y Avg. Value	% Sp Removal	K_L 100 Mesh x 0 K_L 1/2 Inch x 0
4	∿0.8	50	2.7
6	∿0.9	57	3.0
24	∿0.8	75	6.0
48	∿0.9	81	9.6

A sample of 1/4 inch x 0 Lower Kittanning coal was riffled into several narrow size fractions. Pyrite removal data for 100 x 0, 14 x 28, and 4 x 8 mesh fractions are shown in Table 24. The pyritic sulfur removal rates differed substantially, but in all cases high pyritic sulfur removals were obtained. While these size fractions are all observed to react at acceptable pyrite leaching rates (from a commercial processing standpoint) during 102°C processing, the 14 x 28 mesh and 100 mesh x 0 fractions are seen to react at significantly higher rates than the 4 x 8 mesh fraction. These pyrite removal rates may be taken as a relative measure of the fraction of readily accessible pyrite which is associated

TABLE 24. PRELIMINARY DATA ON THE CHEMICAL REMOVAL OF PYRITIC SULFUR FROM SIZE-FRACTIONS OF LOWER KITTANNING COAL AT 102°C

Coal Fraction		Run No.	Time Hours	% w/w Sulfur Forms				Ash	Btu	% Pyrite Removal
Mesh	Wt.			Total	Pyritic	Sulfate	Organic			
1/4"x0	100	-	0*	4.45	3.48	0.50	0.47	20.84	11822	0
		1&2	24	1.68	0.93	0.12	0.63	17.02	12728	73
		3&4	48	1.50	0.66	0.14	0.70	15.54	13023	81
4 x 8*	25	-	0**	5.06	3.95	0.43	0.68	25.44	10927	0
		2	48	2.03	1.29	0.09	0.66	21.86	11970	67
		3	120	1.53	0.57	0.14	0.82	20.30	12032	86
14 x 28*	20	-	0**	3.51	2.46	0.40	0.65	16.56	12643	0
		2	12	1.24	0.53	0.07	0.64	11.82	13693	78
		1	24	1.06	0.30	0.06	0.70	9.13	14129***	88
		1	48	1.08	0.30	0.08	0.70	13.86	13258***	88
		2	72	1.08	0.18	0.10	0.86	12.30	13533	93
100 x 0*	11	-	0**	4.62	2.62	1.02	0.98	20.79	11543	0
		2	6.5	1.50	0.25	0.24	1.01	13.66	13285	90
		2	12	1.38	0.15	0.23	1.00	13.00	13321	96
		1	24	1.19	0.05	0.25	0.89	12.40	13280	98
		1	48	1.23	0.05	0.25	0.93	12.55	13178	98

* Size cuts of 1/4 inch x 0 coal

** Starting coal

***Sampling problem is suspected here

with each size fraction. Thus, it is seen that the finer cuts of coarse coal (those containing pyrite which is largely of the accessible type) would probably be receptive to elevated temperature processing and, perhaps, benefit could be realized by processing these coarse coal fractions in an L-R mode with the coarser cuts being processed at 102°C under ambient pressure.

5. PROCESS ENGINEERING

Process design studies for chemical removal of pyritic sulfur from coal have indicated that the process may be laid out using a number of alternative processing methods. Some of the variations which have been tested and considered in preliminary engineering designs include the following:

- Air vs oxygen for regeneration
- Coal top sizes from 1/4 inch to 100 mesh
- Leaching and regeneration temperatures up to 265°F (130°C)
- Leaching and regeneration in the same vessel and in separate vessels
- Removal of generated elemental sulfur by vaporization or solvent extraction

All of the above conditions are effective and their utilization involves economic trade-offs. Because processing steps and equipment needed for removing sulfur from fine or suspendable coal sizes (up to about 8 mesh top size) are significantly different from those needed for coarser coal, they are separately described, respectively, in Sections 5.1 and 5.2. A summary of projected process economics for commercialization of both fine and coarse coal processes is given in Section 5.3.

5.1 SUSPENDABLE COAL PROCESSING

Suspendable coal is coal of a small enough particle size that it may be processed as a substantially uniform slurry with moderate mixing energy. Although no sharp top size specification can be given, it appears that coals with top sizes up to about 8 mesh may be classed as suspendable. Bench-scale experiments were conducted using 14 mesh and 100 mesh top size coals as representative of the suspendable type. Either of these sizes are often referred to as fine coal to differentiate them from the coarse coal described in Section 5.2.

Preceding page blank

A conceptual full scale process design for the chemical removal of pyritic sulfur from fine coal is described in three sub sections. Section 5.1.1 gives the design basis which relies heavily on the bench-scale experimental data, but also incorporates information provided by equipment vendors and data obtained from the literature. Section 5.1.2 presents the baseline design and equipment list with capital and operating cost estimates. Section 5.1.3 summarizes the major trade-offs examined in arriving at the baseline design and shows some of the cost and operating sensitivities of the process.

5.1.1 Design Basis for Suspendable Coal

Processing coal to remove pyritic sulfur using aqueous iron sulfate involves four major process sections, each containing several unit operations.

The reactor section which includes mixing and solution regeneration has three main process requirements which are:

- Providing mixing and wetting of ground coal with the aqueous ferric sulfate leach solution and raising the slurry to the operating temperature and pressure.

- Providing the residence time and reaction conditions which remove a nominal 95 percent of the pyrite orginally contained in feed coal.

- Providing the residence time and reaction conditions which regenerate the ferric sulfate solution from the spent iron sulfate leach solution.

The washing section which includes several stages of coal washing and coal dewatering has two main process requirements which are:

- Providing for contact of the leach solution-wet coal with a minimum quantity of wash water to remove water soluble iron sulfates.

- Providing for separation of coal from the leach solution and the wash water.

The sulfur removal section which removes both elemental sulfur and excess water from the product coal has four main process requirements which are:

- Providing conditions such as heat or solvent contact to remove elemental sulfur from the processed coal.
- Providing the thermal environment necessary to reduce the moisture level of the coal to the desired value.
- Providing the means for recovery of the elemental sulfur for subsequent marketing, storage or disposal.
- Providing for separation of coal product from solvent, if used.

The sulfate removal section which removes excess iron sulfate from the recycle leach solution has four main process requirements which are:

- Providing for the removal of iron sulfate from the aqueous spent leach solution by crystallization and/or neutralization.
- Providing for the recovery of wash water from the wash section effluents.
- Providing for maintaining the correct acid level by neutralizing excess acid if required.
- Providing for separation of the by-product iron sulfate and neutralization product from the recycle streams.

Specific information and data for the steps or operations which are important to the process design are presented in the following paragraphs. These data rely heavily on the information given in Section 2.7 but also include qualitative observations made during the bench-scale experimental efforts.

Mixing - The present bench-scale effort has demonstrated that there is a more critical aspect to the mixing operation than simply surface wetting the particles and suspending them in the leach solution. Preparing the slurry can be readily accomplished with mixing times of 15 minutes or less, but it was found that severe foaming of the slurry will occur when it is pressurized and raised in temperature. Based on the experience described in Section 2.4.1, the mixing time for a high rank, high ash, dry coal should be between 30 and 60 minutes at the normal boiling point of the solution if subsequent foaming is to be avoided. Lesser times may be possible with moist or low rank coal. The quantity of foam produced seems to decrease with increasing coal particle size and to decrease with lower solids content in the slurry. These are secondary parameters which should not be considered of major importance in the process design.

Leach Reaction - The net overall reaction between pyrite and the ferric sulfate leach solution is represented by:

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \longrightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S \quad (15)$$

$$\Delta H = -55\ \text{Kcal/g-mole}\ FeS_2 = -0.10\ \text{MM btu/lb-mole}\ FeS_2\ \text{reacted}$$

The reaction rate was found to have a second order dependence on both the fraction of pyrite (or pyritic sulfur) in the coal and the fraction of the total iron in the leach solution which is in the ferric ion form. The leach rate at temperatures of interest is represented as follows:

$$r_L = \frac{-d[Wp]}{dt} = K_L\ [Wp]^2\ [Y]^2 \quad (16)$$

where $[Wp]$ = wt% pyrite in dry coal at time t,

$[Y]$ = fraction of iron as ferric ion at time t, and

K_L = leach rate constant (a function of temperature and Wp).

K_L is independent of total iron concentration at least in the immediate vicinity of 3 percent to 5 percent total iron. Physical considerations such as increased solution density and viscosity and the limited solubility of ferrous sulfate in the ferric sulfate solution become increasingly important to the design of the pyrite leacher when total iron concentration approaches 10 percent.

The leach rate constant as a function of temperature can be adequately represented by

$$K_L = A_L \times \exp(-E_L/RT) \quad (17)$$

where E_L = 11,100 cal/mole,
R = 1.987 cal/ mole - °K,
T = temperature in °K, and
A_L = a function of size, temperature and Wp.

For 14 mesh top size coal at atmospheric pressure and temperatures between 70°C and the solution boiling point (about 102°C), the value of A_L is 2.7×10^5 for all values of Wp. At temperatures between 110°C and 130°C under oxygen and steam pressure up to about 150 psig, the value of A_L is 7.4×10^5 when Wp is large (above 1.6) and 2.7×10^5 when Wp is small (below 1.2). Additional refinement of the data in the transition region would be desirable, but an adequate representation of the data can be obtained by a linear decrease in A_L from 7.4×10^5 for Wp = 1.6 to the A_L value of 2.9×10^5 for Wp = 1.2.

For 100 mesh top size coal, the ranges of applicability for A_L appear to be the same, but its value is about 25 percent higher. Thus at low temperature or low Wp, the value of A_L is 3.4×10^5 while at higher temperature and high Wp the value is 8.9×10^5.

These leach rate constants have been defined only for the high pyrite, high ash Lower Kittanning coal used in the bench-scale programs. They should not be applied to other coals or coal seams. The Lower Kittanning coals investigated in the bench-scale programs had starting values for this coal of Wp between 6 and 8. The transition to a lower rate constant, thus, occurs at about 75 percent to 80 percent pyrite removal (Wp ~1.6). Based on a single test of a coal with a lower ash and low starting Wp (Upper Freeport seam, Wp = 1.7), a high leach rate was found at least to 80 percent or 90 percent removal (i.e., Wp about 0.2).

Regeneration - The leach reaction produces both ferrous sulfate and sulfuric acid which must be processed for continuous recycle operation. For each mole of pyrite reacted 9.6 moles of ferrous sulfate must be regenerated to maintain the acid at a constant level. This gives by-products for disposal of 0.2 moles of $Fe_2(SO_4)_3$, 0.6 moles of $FeSO_4$ and 0.8 moles of elemental sulfur. Alternately, regeneration of 9.2 moles of ferrous sulfate can be considered if some acid is neutralized to give by-products of 1.0 mole of $FeSO_4$, 0.2 moles of H_2SO_4 and 0.8 moles of elemental sulfur. The choice of the extent of regeneration should be made on the basis of the by-product preference and economics within process design constraints.

The regeneration reaction is:

$$1.0\ FeSO_4 + 0.5\ H_2SO_4 + 0.25\ O_2 \longrightarrow 0.5\ Fe_2(SO_4)_3 + 0.5\ H_2O \qquad (18)$$

$$\Delta H = -18.6\ \text{Kcal/g-mole}\ FeSO_4 = -.0335\ \text{MM btu/lb-mole}\ FeSO_4$$

If hydrolysis of a portion of the ferric sulfate to iron oxide should occur as

$$Fe_2(SO_4)_3 + 3\ H_2O \longrightarrow Fe_2O_3 + 3\ H_2SO_4, \qquad (19)$$

then additional acid neutralization or regeneration of ferrous ion would be required to remove the acidity produced from the hydrolysis reaction. The extent of hydrolysis at temperatures below 250°F appears to be small, but at higher temperatures there is some evidence of precipitation of ferric oxide and possibly a low hydrate or anhydrous ferrous sulfate. The hydrolysis products and/or precipitates formed at 265°F were found to redissolve slowly in ambient temperature spent leach solution and do not remain as permanent products. No data was obtained above 265°F.

The regeneration rate was found[1] to be second order in the molar concentration of ferrous ion over the range of ferrous concentration from 100 percent to less than 1 percent of the total iron. The rate is

$$r_R = \frac{-d[Fe^{+2}]}{dt} = K_R\ [Fe^{+2}]^2\ [O_2], \qquad (20)$$

where $[Fe^{+2}]$ = concentration of ferrous ion, mole/liter,

$[O_2]$ = oxygen partial pressure, atm, and

K_R = 1.832 liters/mole-atm-hour at 248°F.

Over the range of temperatures studied (212°F to 265°F) the rate constant was found to vary exponentially with temperature as

$$K_R = 40.2 \times 10^6 \exp(-13{,}200/RT), \qquad (21)$$

which gives

Temp., °F (°C)	K_R, liters/mole-atm-hour
212 (100)	0.74
230 (110)	1.18
248 (120)	1.83
266 (130)	2.79

The ferric sulfate regeneration rates were obtained under conditions where oxygen in the form of minute air or oxygen bubbles was dispersed throughout the ferrous sulfate solution. Thus, all of the solution was continually saturated with oxygen at the partial pressure of oxygen present in the regeneration gas. At bench-scale, the minute bubbles were formed by pumping a portion of the liquid in turbulent flow (N_{Re} >3000) through a pipe whose length was 50 or more times its diameter. Gas containing oxygen was added to the liquid in an amount ranging from less than 1 percent to greater than 10 percent by volume at flow conditions. The method is very similar to aeration equipment used to reduce the biological or chemical oxygen demand of chemical plant effluent streams, except that ferric sulfate regeneration is conducted at higher temperatures.

Separation - The major separation step requires treated, fine coal to be separated from the spent leach solution. The four principal methods which could be employed are hydrocyclones, centrifuges, filters and thickeners. Suspendable coal has a large fraction of particles smaller than 100 microns in diameter and in general hydrocyclones are not useful for particle sizes below several hundred microns. Centrifuges would require very high power input and recycle rates to separate the coal from the leach solution because of the fine particle size and the small liquid-solid density difference. Filtration is applicable, but for slurries less than 30 or 35 percent solids, the filter area requirements increase rapidly. Typically, a 10 percent solids slurry needs more than ten times the filter area needed for a 35 to 55 percent slurry. Thickeners have been used on commercial scale to remove coal fines from water and other aqueous media. Data for similar density solutions and coal sizes were reported in Reference 4. It was estimated that a thickener area of about 20 ft^2 per ton/day of coal with an edge depth of about 8 feet would provide an underflow with greater than 35 percent solids and an overflow containing only a few tenths percent (or less) solids when the feed contains 10 to 20 percent of 100 mesh coal. Since the thickener slurry can be maintained near the leach solution boiling point, the time spent in the thickener could be used to carry the leaching reaction to greater degree of completion and to redissolve any solids formed during leaching/regeneration.

Filtration - The two important design values relating to filtration are the filtration rate and the coal "moisture" content. These values are not independent and are both highly dependent on the specific coal and its properties. Generalized correlations reported in the literature were reviewed and a data point was obtained from a filter manufacturer for a bench-scale slurry of the high ash, Lower Kittanning coal. The vendor report given in Appendix F showed that rates equivalent to about 25 lb of dry coal/hr/ft^2 were obtained with a 20 percent slurry of -100 mesh coal in a 5 percent iron leach solution. They projected a 60 percent increase in rate for a slurry with a solids concentration of about 33 percent.

One reported correlation[5] plots rate against a parameter which is the product of the percent ash in the -200 mesh fraction times the square root of the weight percent of the -200 mesh fraction. For the Lower Kittanning sample tested in the above filtration test, the parameter has a value of about 200:

$$(25\%\ \text{ash}) \times (67\%\ \text{of}\ -200)^{1/2} = 205$$

Figure 22 shows this measured point and the literature data with extrapolations to a typical 14 mesh top size coal. The expected filtration rate for a cleaned 14 mesh top size coal is expected to be near 200 $lb/hr/ft^2$ in a 33 percent slurry and about 150 $lb/hr/ft^2$ in a 20 percent slurry. For a cleaned 100 mesh top size coal the filtration rate is expected to be about 100 $lb/hr/ft^2$ for a 33 percent slurry and about 70 $lb/hr/ft^2$ for a 20 percent slurry.

Data on the moisture content of the filter cake was taken by the filter manufacturer at the same time as rate was measured. Appendix F shows the projected cake moisture to be 40 to 45 percent. This is higher than either reported in the literature (26 to 34%) or found in a typical bench-scale filtration (about 32%) for the high ash, 100 mesh top size coal. The literature values are for water wet rather than leach solution wet cakes. The data for both water and leach solution (5 to 5.5% iron) are summarized as follows:

	parts of liquid per 100 parts of dry coal	
	100 mesh high ash	14 mesh high ash
Bench Scale		
leach solution	45-50	45-50
water	35-40	35-40
Vendor Test		
leach solution	65-80	not tested
Reference 5		
water	35-50	15-25

In order to provide for an adequate amount of coal washing to remove the sulfate leach solution it was decided that 50 parts of liquid per 100 parts of dry coal would be used for both leach solution and water on both coal sizes.

5.1.2 Process Baseline Design

A block diagram of the Meyers Process as applied to coal of about 8 mesh top size or finer is shown in Figure 23. The block diagram shows the main

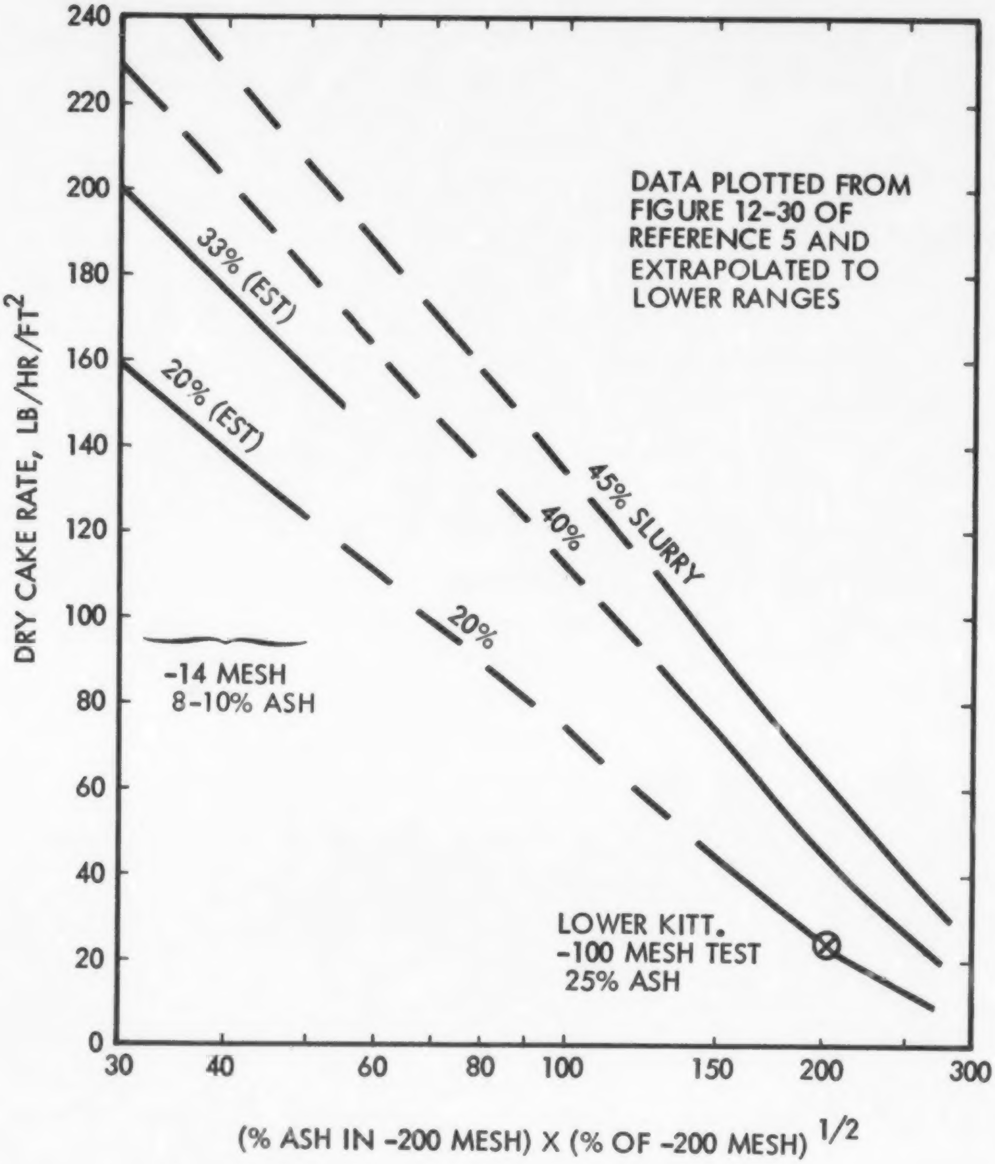


Figure 22. Filtration Rate Correlation

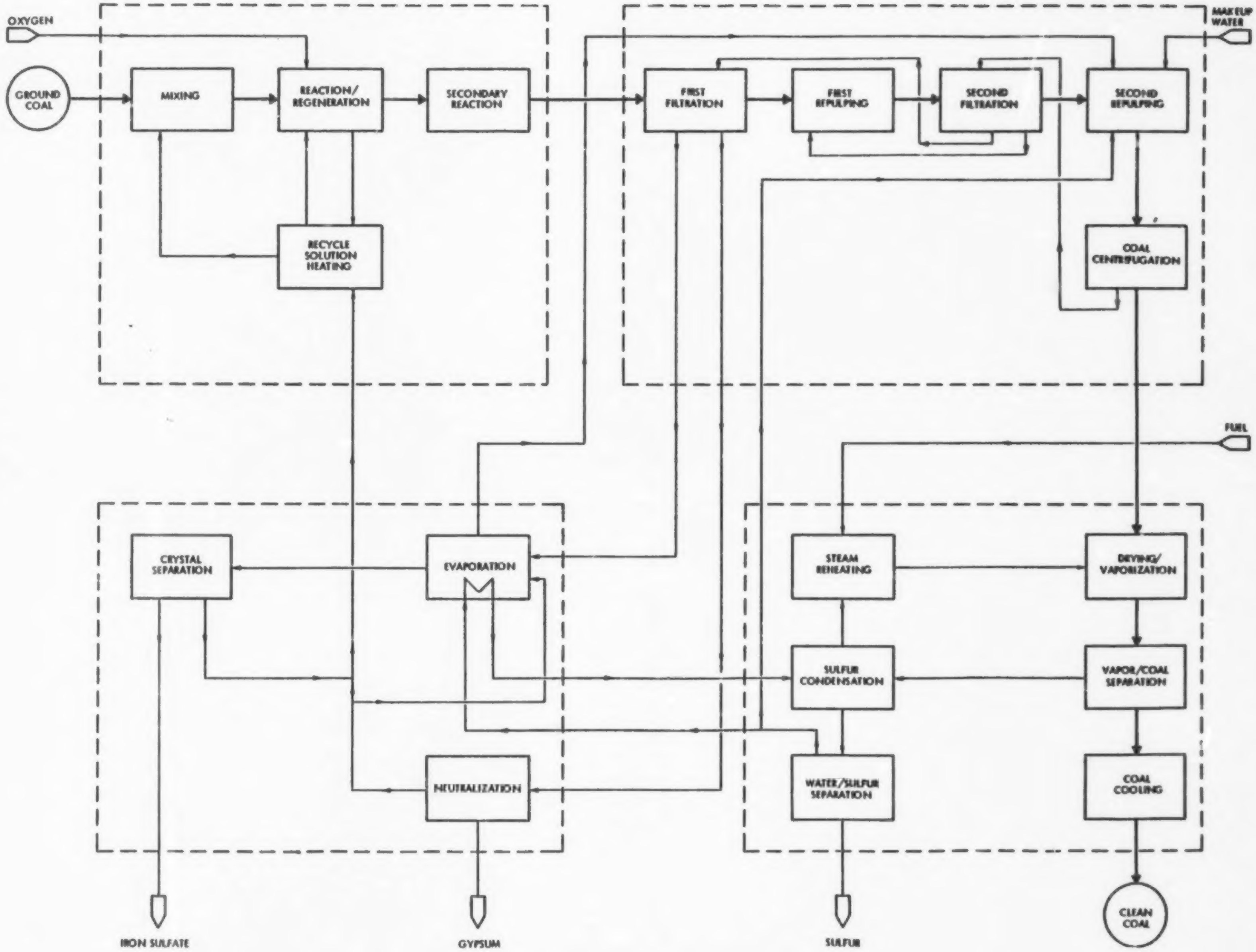

OXYGEN
GROUND COAL
MIXING
REACTION/ REGENERATION
SECONDARY REACTION
RECYCLE SOLUTION HEATING
FIRST FILTRATION
FIRST REPULPING
SECOND FILTRATION
SECOND REPULPING
MAKEUP WATER
COAL CENTRIFUGATION
FUEL
CRYSTAL SEPARATION
EVAPORATION
NEUTRALIZATION
STEAM REHEATING
SULFUR CONDENSATION
WATER/SULFUR SEPARATION
DRYING/ VAPORIZATION
VAPOR/COAL SEPARATION
COAL COOLING
IRON SULFATE
GYPSUM
SULFUR
CLEAN COAL

Figure 23. Block Diagram for Fine Coal

operations and the interconnections between each of the four process sections. Before discussing the process flow diagrams and mass balance in detail, the block diagram will be described to give a brief process overview.

Reactor Section - Ground coal, with a nominal top size of 14 mesh, is mixed with hot recycled iron sulfate leach solution. After wetting is complete at the solution boiling temperature, the slurry is introduced into a vessel where the majority of the pyrite reaction is accomplished at elevated temperature and pressure. Oxygen is simultaneously added to regenerate the leach solution. Heat of reaction is removed and is used to reheat the recycle leach solution. The slurry is passed to a secondary reactor operated at atmospheric pressure and near the solution boiling temperature, where the remaining pyrite reaction occurs.

Wash Section - The iron sulfate leach solution is removed from the powdered coal in a series of counter current flow contactors and separators. The slurry from the secondary reactor is first filtered and the cake is washed on the filter. Both the filtrate and wash liquids are sent to the Sulfate Removal Section. The first filter cake is reslurried, filtered a second time,and then reslurried with recovered clean water and finally dewatered in a centrifuge.

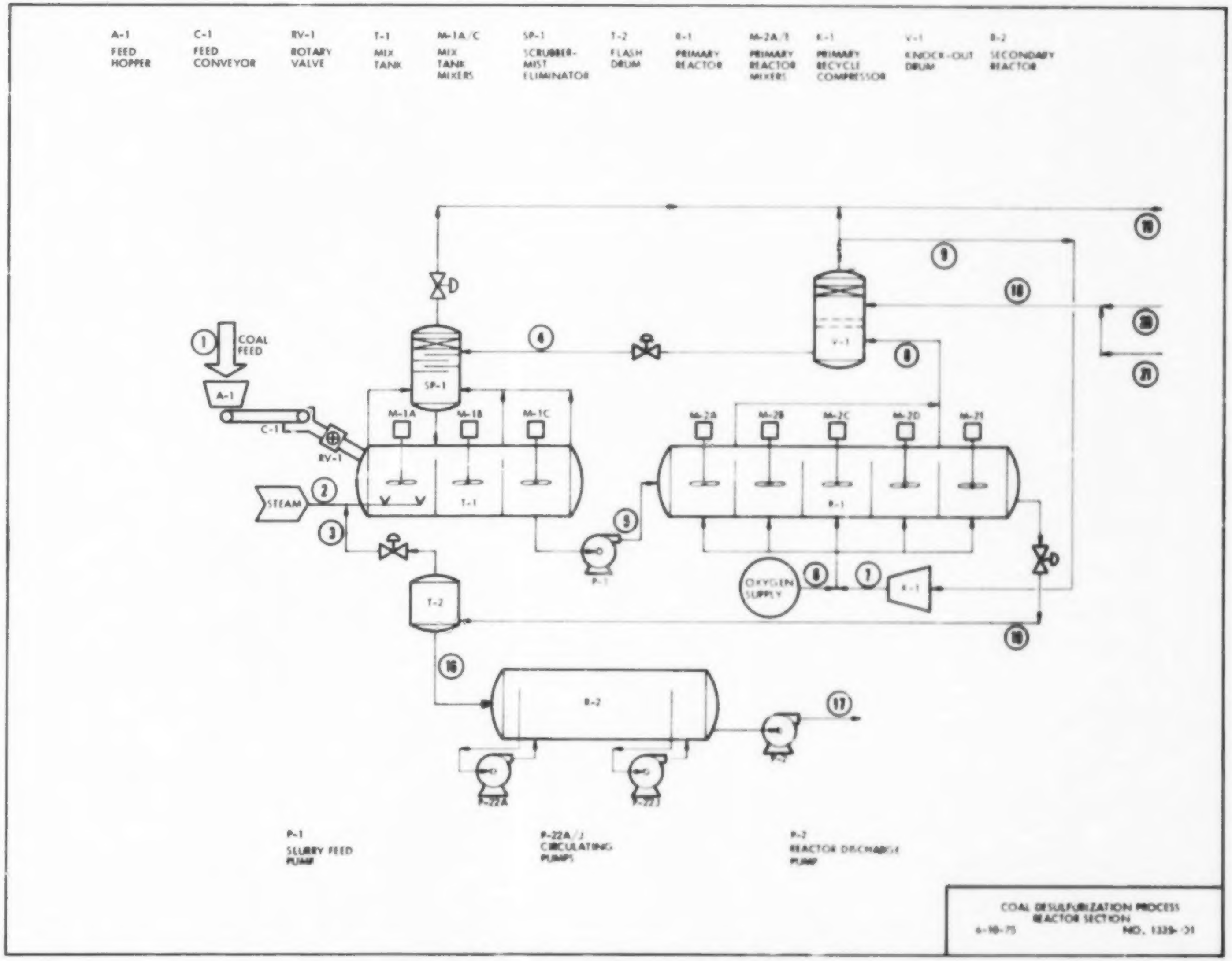
Sulfur Removal Section - Moist coal from the centrifuge is flash dried by high temperature steam which simultaneously vaporizes the elemental sulfur produced in the leach reaction. The dry coal is separated from the hot steam and sulfur vapor stream in a cyclone and cooled to give the clean product coal. The hot sulfur vapor-steam effluent from the cyclone is scrubbed with large quantities recycled hot water and the liquid sulfur is drawn off to by-product storage. A small part of the hot water is used in the Wash Section with the remainder circulated to the evaporator.

Sulfate Removal Section - The major function of this section is the evaporation of wash water to concentrate leach solution for recycle. The filtrate from the wash section and a portion of the spent wash water from the first filter is fed to a three effect evaporator which recovers most of the wash water. The by-product iron sulfate crystals which form in the final stage of evaporation are separated from the concentrated leach solution and stored. The remaining wash water from the first filter is partially neutralized with lime to yield a gypsum by-product. The separated and partially neutralized wash water is combined with the concentrated solution from the crystal separator and recycled to the Reactor Section. Overall, the pyrite is reacted with oxygen and water to give ferrous sulfate, sulfuric acid and sulfur. These by-products are removed as shown. The fuel requirement is equal to a few percent of the product coal and makeup water is needed to replace water of crystallization and water vapor loss through the vacuum filters and the vacuum evaporator.

5.1.2.1 Conceptual Design for Commercial Scale

Process engineering studies and trade-offs produced a baseline flow diagram for a commercial scale plant. The flow sheet, which is divided into its four major sections is given in Figure 24. The corresponding mass balance and stream properties are given in Table 25. The baseline plant size was chosen equal to 100 tons of dry coal feed per hour equivalent to about 250 MW power plant feed. This size is about the maximum size for a single train based on available commercial equipment.

Feed and Mixer - Crushed coal, nominally 14 mesh top size, is feed from feed hopper A-1. The coal is assumed to have 3.2 percent pyritic sulfur and 10 percent moisture on a dry basis; thus, the total solids feed rate is 110 tons per hour (TPH) at room temperature, assumed to be 77°F. The coal feed, stream 1, is brought to the mix tank, T-1, by conveyor, C-1, and introduced through the rotary feed valve, RV-1. Recycled leach solution, stream 4, at its boiling point (215°F) is introduced to the first mixer stage after first passing through the gas scrubber SP-1. Steam, streams 2 and 3, is needed to raise the feed coal from 77°F to the 215°F mixer temperature. Approximately 5.6 TPH of atmospheric pressure steam is required to heat the coal while 6.5 TPH is available from the flash drum, T-2. It is possible that the steam would actually be added to the enclosed conveyor to provide heated coal with an effective 15.6 percent moisture content. The excess 0.9 TPH would be vented through SP-1 along with any flash steam formed in stream 4.



A-1 FEED HOPPER
C-1 FEED CONVEYOR
RV-1 ROTARY VALVE
T-1 MIX TANK
M-1A/C MIX TANK MIXERS
SP-1 SCRUBBER-MIST ELIMINATOR
T-2 FLASH DRUM
R-1 PRIMARY REACTOR
M-2A/I PRIMARY REACTOR MIXERS
K-1 PRIMARY RECYCLE COMPRESSOR
V-1 KNOCK-OUT DRUM
R-2 SECONDARY REACTOR
COAL FEED
STEAM
OXYGEN SUPPLY
M-1A
M-1B
M-1C
M-2A
M-2B
M-2C
M-2D
M-2I
SP-1
V-1
T-1
R-1
T-2
R-2
K-1
P-1
P-22A
P-22J
P-2
1
2
3
4
5
7
8
9
16
17
P-1 SLURRY FEED PUMP
P-22A/J CIRCULATING PUMPS
P-2 REACTOR DISCHARGE PUMP
COAL DESULFURIZATION PROCESS
REACTOR SECTION
6-10-75
NO. 1335-31

Figure 24. Process Flow Diagram for Fine Coal

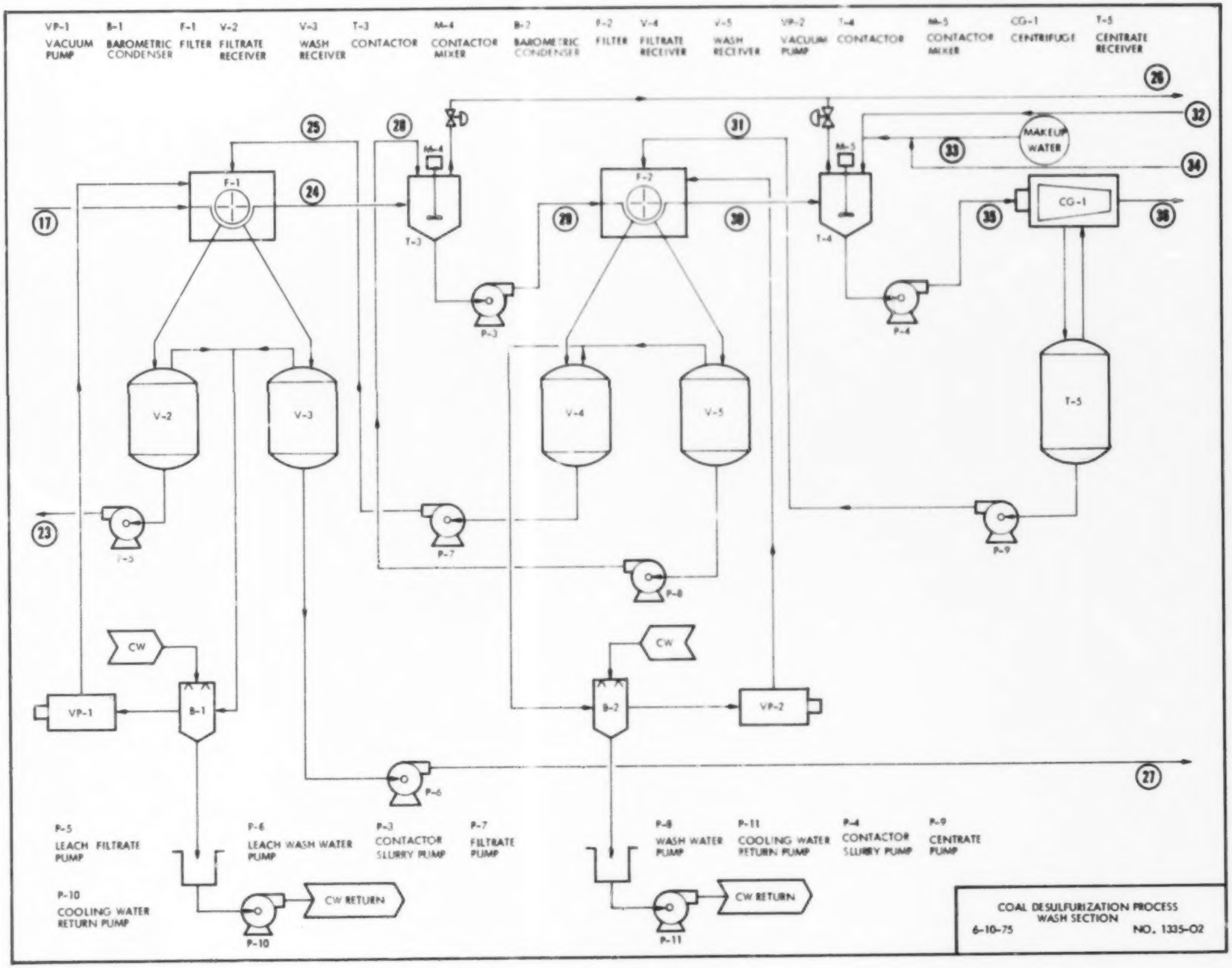

VP-1 VACUUM PUMP
B-1 BAROMETRIC CONDENSER
F-1 FILTER
V-2 FILTRATE RECEIVER
V-3 WASH RECEIVER
T-3 CONTACTOR
M-4 CONTACTOR MIXER
B-2 BAROMETRIC CONDENSER
F-2 FILTER
V-4 FILTRATE RECEIVER
V-5 WASH RECEIVER
VP-2 VACUUM PUMP
T-4 CONTACTOR
M-5 CONTACTOR MIXER
CG-1 CENTRIFUGE
T-5 CENTRATE RECEIVER
17
23
24
25
26
27
28
29
30
31
32
33
34
35
36
MAKEUP WATER
CW
CW RETURN
P-5 LEACH FILTRATE PUMP
P-6 LEACH WASH WATER PUMP
P-3 CONTACTOR SLURRY PUMP
P-7 FILTRATE PUMP
P-8 WASH WATER PUMP
P-11 COOLING WATER RETURN PUMP
P-4 CONTACTOR SLURRY PUMP
P-9 CENTRATE PUMP
P-10 COOLING WATER RETURN PUMP
COAL DESULFURIZATION PROCESS
WASH SECTION
6-10-75
NO. 1335-02

Figure 24. (Continued)

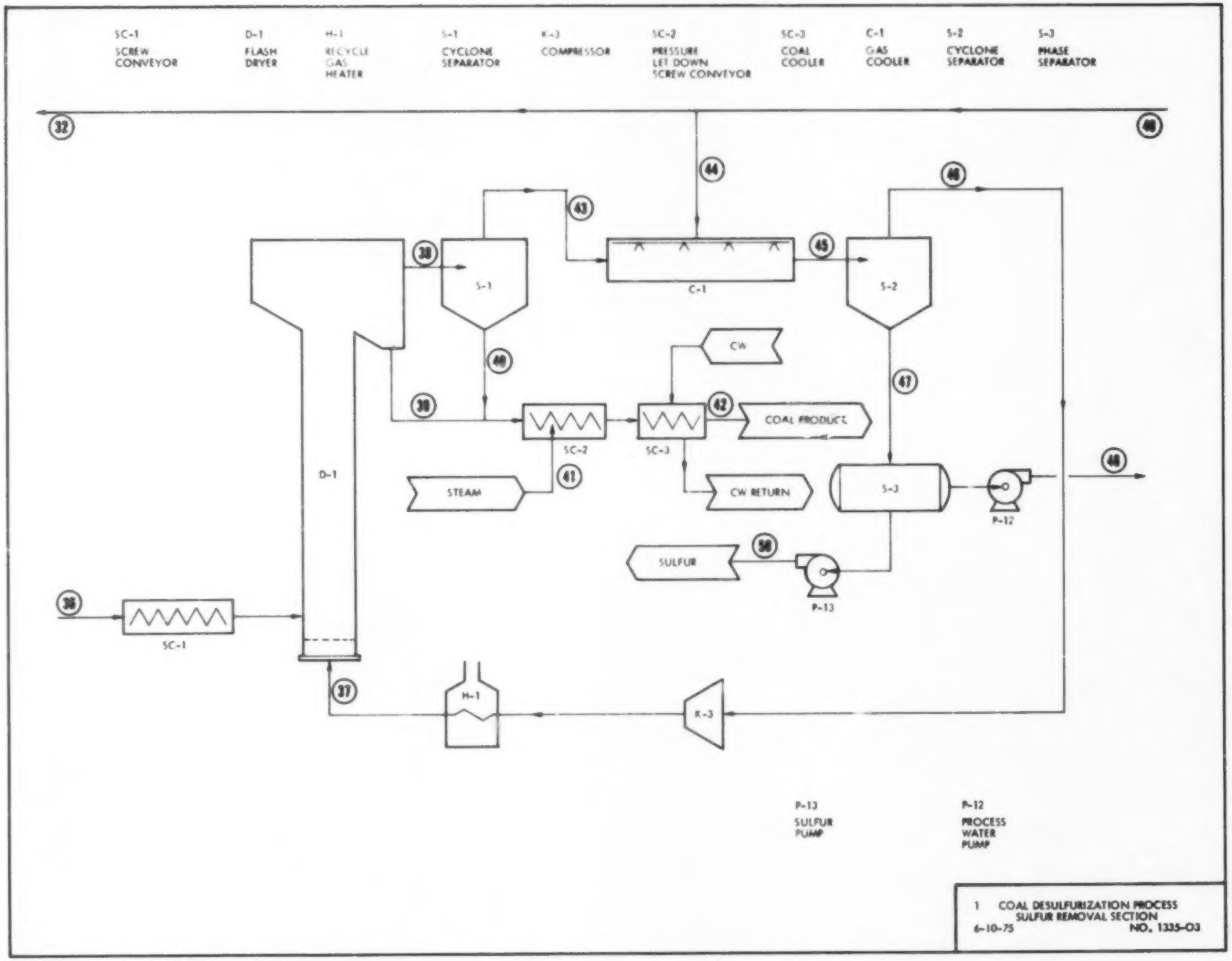

SC-1
SCREW CONVEYOR
D-1
FLASH DRYER
H-1
RECYCLE GAS HEATER
S-1
CYCLONE SEPARATOR
K-3
COMPRESSOR
SC-2
PRESSURE LET DOWN SCREW CONVEYOR
SC-3
COAL COOLER
C-1
GAS COOLER
S-2
CYCLONE SEPARATOR
S-3
PHASE SEPARATOR
32
44
46
43
38
S-1
45
C-1
S-2
40
CW
47
39
SC-2
SC-3
42
COAL PRODUCT
D-1
STEAM
41
CW RETURN
S-3
P-12
48
SULFUR
50
P-13
36
SC-1
37
H-1
K-3
P-13
SULFUR PUMP
P-12
PROCESS WATER PUMP
1 COAL DESULFURIZATION PROCESS
SULFUR REMOVAL SECTION
6-10-75
NO. 1335-O3

Figure 24. (Continued)

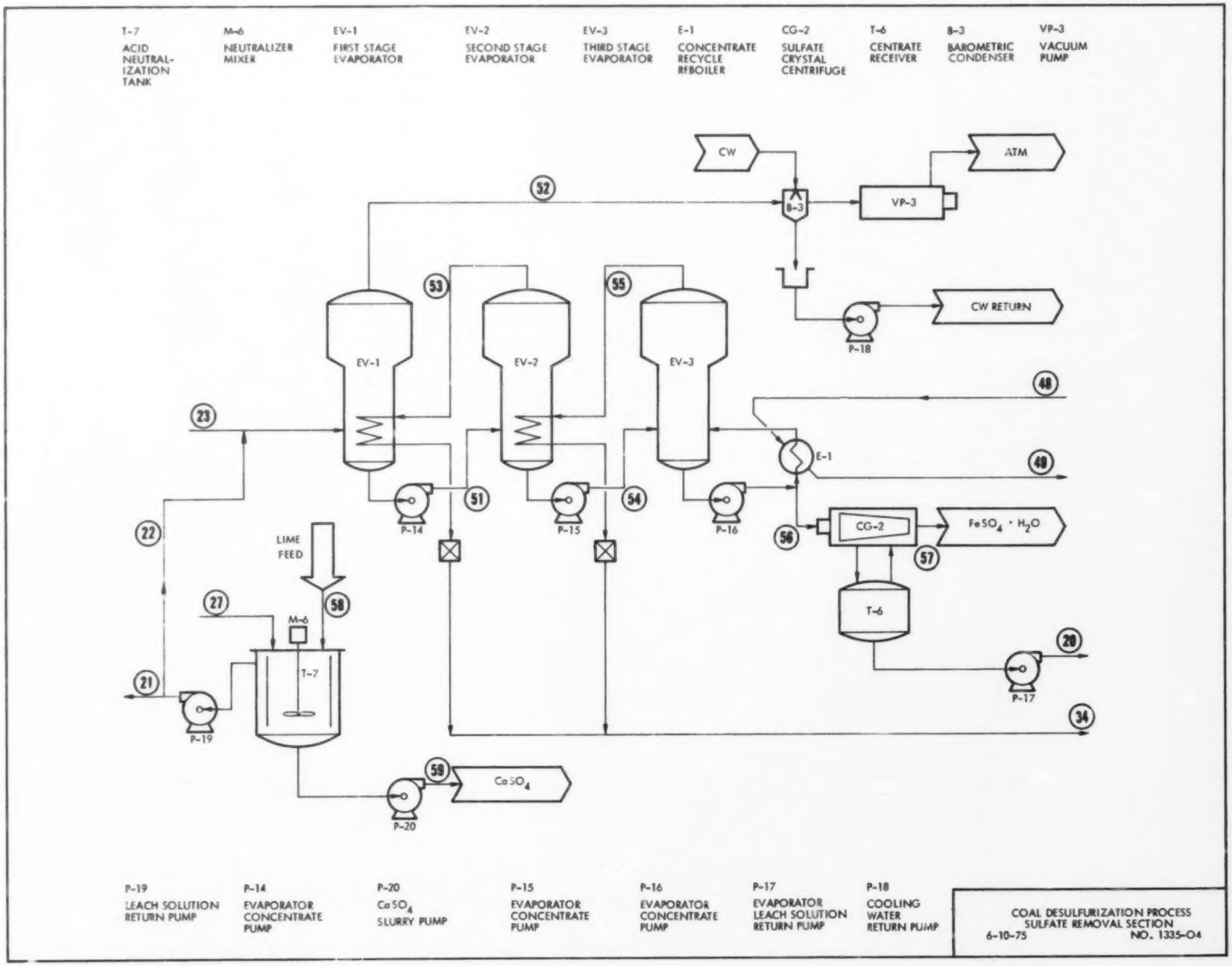

T-7
ACID NEUTRALIZATION TANK
M-6
NEUTRALIZER MIXER
EV-1
FIRST STAGE EVAPORATOR
EV-2
SECOND STAGE EVAPORATOR
EV-3
THIRD STAGE EVAPORATOR
E-1
CONCENTRATE RECYCLE REBOILER
CG-2
SULFATE CRYSTAL CENTRIFUGE
T-6
CENTRATE RECEIVER
B-3
BAROMETRIC CONDENSER
VP-3
VACUUM PUMP
CW
ATM
52
VP-3
B-3
53
55
CW RETURN
P-18
EV-1
EV-2
EV-3
48
23
E-1
49
51
54
P-14
P-15
P-16
56
CG-2
$FeSO_4 \cdot H_2O$
57
22
LIME FEED
27
58
M-6
T-6
20
21
T-7
P-19
P-17
34
59
$CaSO_4$
P-20
P-19
LEACH SOLUTION RETURN PUMP
P-14
EVAPORATOR CONCENTRATE PUMP
P-20
$CaSO_4$ SLURRY PUMP
P-15
EVAPORATOR CONCENTRATE PUMP
P-16
EVAPORATOR CONCENTRATE PUMP
P-17
EVAPORATOR LEACH SOLUTION RETURN PUMP
P-18
COOLING WATER RETURN PUMP
COAL DESULFURIZATION PROCESS
SULFATE REMOVAL SECTION
6-10-75
NO. 1335-04

Figure 24. (Continued)

TABLE 25. PROCESS MASS BALANCE FOR FINE COAL
(Stream Flows in Tons Per Hour)

	COAL FEED	MAKEUP STEAM	FLASH STEAM	FEED SOLN.	R-1 FEED	O_2 MAKEUP	RECYCLE GAS	R-1 GAS	COMPRESSOR FEED	R-1 EXIT	R-2 FEED	R-2 EXIT
	1	2	3	4	5	6	7	8	9	10	16	17
Water	10.0	-.9*	6.5	144.1	159.2		1.5	14.0	1.5	147.4	140.9	140.7
$FeSO_4$				3.9	14.4					5.8	5.8	11.1
$Fe_2(SO_4)_3$				30.6	18.2					37.0	37.0	30.6
H_2SO_4				5.7	8.8					5.0	5.0	6.6
Pyrite	6.0				5.2					.7	.7	.3
Sulfur					.2					1.1	1.1	1.2
Coal	94.0				94.0					94.0	94.0	94.0
Oxygen						3.9	13.1	13.4	13.1			
Inert						Tr	.8	.8	.8			
Total, TPH	110.0	-0.9	6.5	134.4	300.0	3.9	15.3	28.2	15.3	291.0	284.5	284.5
T, °F	77	215	215	215	215	77	264	250	177	250	215	215
P, Psig	0	.9	.9	0	28.8	53.8	53.8	28.8	28.8	28.8	0	0
gpm	-	-	-	614	968	-	-	-	-	907	873	874
ρ, lb/ft^3	50.0	-	-	74.8	77.3	-	-	-	-	80.0	81.3	81.2
Fe, %	-	-	-	5.4	5.2	-	-	-	-	6.3	6.6	6.7
Y	-	-	-	.86	.49	-	-	-	-	.83	.83	.68
SO_4/Fe	-	-	-	1.75	1.73	-	-	-	-	1.64	1.64	1.64

*Excess steam to vent

TABLE 25. (CONTINUED)

	Return Soln.	Vent O_2	Crystallizer Centrate	Neutralizer Return	Neutralizer to Crystallizer	Filtrate to Crystallizer	Cake F-1	Wash F-1	Contactor Vents	To Neutralizer	Contractor Feed T-3	F-2 Feed Slurry
	18	19	20	21	22	23	24	25	26	27	28	29
Water	131.7	Tr	50.3	81.4	54.3	105.2	43.1	143.1	Tr	135.5	146.3	189.4
$FeSO_4$	3.9		2.2	1.7	1.1	8.3	1.0	1.0		2.8	.3	1.3
$Fe_2(SO_4)_3$	30.6		26.0	4.6	3.1	22.9	3.0	3.0		7.7	.9	3.9
H_2SO_4	5.7		5.2	.5	0.3	4.9	.6	.6		1.7	.2	.8
Pyrite							.3					.3
Sulfur							1.2					1.2
Coal							94.0					94.0
Oxygen		.4										
Inert		Tr										
Total, TPH	171.9	0.4	83.7	88.2	58.8	141.3	143.2	147.7	0.0	147.7	147.7	290.9
T, °F	127	177	200	160	160	160	160	160	77	160	160	160
P, Psig	28.8	0	30.0	15.0	15.0	10.0	0	10.0	0	5.0	5.0	15.0
gpm	548	-	221	335	224	443	-	589	-	561	601	1065
ρ, lb/ft^3	78.2	-	95.4	65.6	65.6	79.6	-	62.5	-	65.7	61.3	68.1

TABLE 25. (CONTINUED)

	Cake F-2	Wash F-2	Dryer Water Return	Makeup Water	Evaporator Return	Centrifuge Feed Slurry	Cake Centrifuge	Dryer Gas	Dryer Output	Dryer Coarse Cut	Cyclone Solids	Purge Steam	Coal Product	Cyclone Gas	Cooler Water Feed
	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44
Water	47.2	147.2	14.3	27.1	72.9	161.5	14.3	258.9	273.2	Tr	Tr	0.1	0.1	273.2	1137.4
$FeSO_4$	.1	.1				.1	Tr		Tr	Tr	Tr		Tr		
$Fe_2(SO_4)_3$	.3	.3				.3	Tr		Tr	Tr	Tr		Tr		
H_2SO_4	.1	.1				.1	Tr		Tr	Tr	Tr		Tr		
Pyrite	.3					.3	0.3		0.1	0.2	0.1		0.3		
Sulfur	1.2					1.2	1.2	Tr	1.2	Tr	Tr		Tr	1.2	
Coal	94.0					94.0	94.0	Tr	41.4	52.6	41.3		93.9	.1	
Oxygen															
Inert															
Total, TPH	143.2	147.7	14.3	27.1	72.9	257.5	109.8	258.9	315.9	52.8	41.4	0.1	94.3	274.5	1137.4
T, °F	160	160	215	77	180	180	180	650	450	450	450	300	150	450	215
P, Psig	0	10.0	30.0	30.0	30.0	15.0	0	20.0	18.0	18.0	18.0	18.0	0	17.8	30.0
gpm	-	607	60	108	473	942	-	-	-	-	-	-	-	-	4745
ρ, lb/ft^3	-	60.7	59.8	62.3	60.2	68.2	-	-	-	-	50.0	-	50.0	-	59.8

TABLE 25. (CONTINUED)

	Cooler Effluent	Separator Gas Effluent	Separator Liquid	Crystallizer Reboiler Feed	Water Return	Sulfur Product	Liq. From EV-1	Steam to Vacuum	Steam From EV-2	Liq. From EV-2	Steam From EV-3	Centrifuge Feed	Sulfate Product	Lime	Calcium Sulfate
	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59
Water	1410.6	258.9	1151.7	1151.7	1151.7		124.1	35.4	35.2	88.9	37.7	51.2	0.9	0.4	
$FeSO_4$							9.4			9.4		9.4	7.2		
$Fe_2(SO_4)_3$							26.0			26.0		26.0			
H_2SO_4							5.2			5.2		5.2			
Pyrite															
Sulfur	1.2	Tr	1.2			1.2									
Coal	.1	Tr	.1			0.1									
Oxygen															
Inert															
Lime														0.5	
Gypsum															1.6
Total, TPH	1411.9	258.9	1153.0	1151.7	1151.7	1.3	164.7	35.4	35.2	129.5	37.7	91.8	8.1	0.9	1.6
T, °F	250	250	250	250	215	215	120	115	150	155	207	210	200	77	77
P, Psig	15.0	15.0	15.0	40.0	30.0	25.0	5.0	(1.5 Psia)	(3.7 Psia)	5.0	(13 Psia)	5.0	0	0	5.0
gpm	-	-	4851	4851	4802	2.9	516			376		230	-	-	2.8
ρ, lb/ft^3	-	-	59.2	59.2	59.8	112.0	79.6	-	-	85.9	-	99.7	-	-	144.8

The mixer vessel T-1 was sized for three stages of mixing at 0.25 hours per stage. Under the design constraint that the vessel is 75 percent full, the cost model used for vessel sizing found a field fabricated vessel 18.7 feet in diameter by 32.9 feet long has minimum cost. The selected vessel size (18 x 36) gives three stages each about 12 feet long and 12.6 feet deep with slightly less than 15000 gallons in each stage. Any foam generated during coal wetting will be broken down and the entrapped air will be scrubbed in SP-1 by the returning leach solution. The actual air flow through SP-1 is very low and will probably not exceed the air in the bulk coal (50 cubic feet per minute).

Primary Reactor - The fully wetted and deaerated coal slurry from the mixer is pumped by slurry pump P-1 (stream 5) into the first stage of the primary reactor R-1. Both removal of pyrite and oxidation of ferrous to ferric iron sulfate occur in this reactor. A five stage reactor was selected since the cost model showed the minimum cost field fabricated vessel had length to diameter ratios near five. Under the design constraint that the reactor must have five stages and operates about 85 percent full, the cost model found a reactor 25.9 feet in diameter by 127.7 feet long operated at 15 psi of oxygen was minimum cost. The selected vessel size (26 x 125) gives five stages each about 25 feet long by 23 feet deep and holding about 80,000 gallons of slurry. At the residence time of 1.5 hours per stage, a temperature of 250°F and an oxygen partial pressure of 15 psi, the pyrite is reduced to 88 percent of the original level and the leach solution is regenerated to a Y (ferric iron to total iron ratio) of 0.83 in the primary reactor.

Oxygen Loop - Excess oxygen saturated with steam and containing an equilibrium level of inert gas (mainly argon) leaves the primary reactor in stream 8. The gas is contacted with returning leach solution, stream 18, in a knock-out drum, vessel V-1. The leach solution is warmed to 215°F (stream 4) by condensing steam from the oxygen stream. The gaseous effluent, which was assumed to leave V-1 50°F warmer than the feed leach solution is split to give a small vent stream 19 and a recycle oxygen stream 9. The vent rate is selected to maintain the inert gas at the design level; namely 5 percent on a dry basis. The recycle oxygen is compressed by K-1 to the reactor feed pressure. Makeup oxygen, stream 6, is added to balance the oxygen used for regeneration in R-1 and that vented to remove inerts.

Assuming 15 psia oxygen pressure the gas pressures in reactor R-1 at 250°F are as follows:

Oxygen	15.0 psia
Inert Gas	.8 psia
Steam	27.7 psia
	43.5 psia (28.8 psig)

Since the recycle gas must also overcome the liquid head in the reactor (about 13 psi), the control valve/injector drop (about 10 psi) and other line losses, the recycle compressor was sized to provide a 25 psi pressure increase. For the baseline case this results in a 300 horsepower compressor operating at a 1.58 compression ratio and a compressor outlet pressure of 53.8 psig.

Flash Steam - The heat of reaction and regeneration is accommodated in three ways: temperatures of the recycled oxygen and the feed slurry are raised in R-1, heat is lost from the insulated walls of the mixer and reactors, and water is evaporated from the solutions. Part of the steam (13.4 TPH) is removed from the recycle oxygen to provide an isothermal primary reactor R-1 at 250°F and part of the steam (6.5 TPH) is removed by flash drum T-2 in dropping the slurry temperature and pressure from reactor R-1 (250°F) to reactor R-2 (215°F). The heat is almost entirely utilized in heating the feed coal and the recycle leach solution.

Secondary Reactor - The secondary reactor, R-2, is operated near the atmospheric boiling point with a residence time of 36 hours. During this time, additional pyrite is removed from the coal to provide an overall pyrite removal of 95 percent while the Y of the solution is decreased to a value of 0.68 in the reactor effluent. The low value of Y is desired to provide sufficient ferrous sulfate for removal as the by-product iron form. The cost model found the minimum cost reactor was 27.9 feet in diameter by 465.9 feet long. The final equipment list and costing used three field fabricated vessels each 28 feet in diameter and 160 feet long. The reactors contain no internal stages, but have circulating pumps to avoid large vertical concentration gradients from occurring in the solution. The slurry from the secondary reactor, stream 17, is pumped by P-2 to the first filter, F-1.

Coal Washing - Bench-scale experience with removal of the sulfate leach solution from coal shows that the solution may be treated as consisting of two types. Surface solution is readily removed by flushing with water or may be readily displaced by a more dilute wash solution. Solution in the pores of the coal particles requires a definite residence time to reach equilibrium with the bulk or surface liquid. The coal washing section, therefore, consists of filtration, washing on the filter, equilibration with dilute solution, a second filtration and wash, equilibration with wash water and finally dewatering in a centrifuge.

First Filter - Coal slurry from the secondary reactor, stream 17, containing approximately 33 percent solids is fed to a 12 foot diameter by 24 foot long rotary vacuum filter, F-1. The filtrate from vacuum receiver V-2, stream 23, is pumped, P-5, to the sulfate removal section. Dilute wash solution from the second filter, stream 25, is used to wash the filter cake and displace the surface solution on the coal particles. This sulfate rich wash solution, stream 27, is pumped, P-6, from the vacuum receiver V-3 to the sulfate removal section. Vacuum is provided by a 3000 standard cubic feet per minute (SCFM) vacuum pump, VP-1, which is vented, stream 26, back to the enclosed filter F-1. The vapors and gases removed from the vacuum receivers, V-2 and V-3, pass through a barometric condenser, B-1, before entering the vacuum pump. In B-1 most of the flash steam is condensed and enters the cooling water loop where it is pumped to the cooling water tower by P-10.

First Stage Repulping - The washed filter cake from the first filter, stream 24, and dilute wash water from the second filter are gravity fed through a closed chute to a stirred tank, T-3. This 40,000 gallon tank is operated about three-fourths full to give an average residence time of 30 minutes to equilibrate pore solution with the bulk liquid. The slurry, stream 29, is pumped, P-3, to the second stage filter. Any gases introduced with the cake are vented to the scrubbing system, stream 26.

Second Filter - The partially washed slurry, stream 29, containing approximately 33 percent solids, is filtered and washed on a second filter of the same size and type as the first filter. Filtrate, stream 25, is pumped, P-7, from the vacuum receiver, V-4, to the first filter wash. Wash water for the second filter, stream 31, is obtained from the centrate receiver. The partially spent wash water is pumped, P-8, from the vacuum receiver V-5 to the first stage contactor. Vacuum is provided by vacuum pump VP-2 operating through the barometric condenser B-2.

Second Stage Repulping - The washed filter cake from the second filter, stream 30, is contacted with water in a 40,000 gallon stirred tank, T-4. The wash water, streams 32, 34, and 33 is obtained from the dryer, the evaporators, and makeup, respectively.

Dewatering - The slurry from the second contactor, stream 35, is pumped, P-4, to the dewatering centrifuge, CG-1. The slurry with approximately 33 percent solids is separated in the 36 inch diameter by 90 inch long solid bowl centrifuge to provide a dewatered coal, stream 36. According to vendor literature and discussions, the dewatered coal is expected to have about 15 percent moisture. The centrate from receiver T-5 is pumped, P-9, to provide the wash, stream 31, for the second filter.

Drying - Coal from the centrifuge, stream 36, is fed to a flash dryer, D-1, by a screw feeder, SC-1. In this dryer concept the coal is heated to about 450°F by superheated steam, stream 37, and carried upward to the enlarged top area of the dryer. The larger particles are removed from the dryer, stream 39, while the fine particles and gas, stream 38, are fed to a cyclone, S-1. During the drying in D-1 sulfur is also vaporized from the coal and is present along with water vapor in the cyclone effluent gas stream 43. Thefine coal from the cyclone, stream 40, and coarse coal, stream 39, are let down to atmospheric pressure by screw conveyor SC-2 which is back purged with a small quantity of steam to prevent the sulfur containing gas in the cyclone from leaving the system with the coal. The coal, stream 42, is then transported and cooled to product storage temperature by the screw conveyor, SC-3 which rejects heat either to cooling water or to the atmosphere.

Sulfur Removal - The cyclone effluent gas, stream 43, at about 450°F is cooled by a large spray of water, stream 44, in gas cooler C-1. The water is obtained from return stream 49 from the sulfate removal section. The gas and liquid, stream 45, cooled to 250°F is separated in cyclone S-2 to give vapor stream 46 and liquid stream 47. The liquid stream 47 contains the water fed to the gas cooler, stream 44, the water vaporized from the coal in the dryer, and the sulfur vaporized from the coal. The liquid is phase separated in vessel S-3. The liquid sulfur by-product, stream 50, is pumped, P-13, to storage while the hot water, stream 48, is pumped, P-12, to the sulfate removal section.

Steam Circulation - Saturated steam at 250°F from the cyclone, stream 46, is compressed by K-3, reheated by H-1, and fed to the dryer as stream 37. Compression is accomplished by two 3500 HP series compressors which make up the 10 psi pressure drop around the gas circulation loop. The heater provides nearly 100 million Btu per hour (MM Btu/hr) to the steam to supply the heat required to heat the dryer feed, stream 36, to 450°F and vaporize the water and sulfur. Slightly more than 80 MM Btu/hr are rejected to the hot water loop, stream 48, for use in the sulfate removal section while about 15 MM Btu/hr are lost from the equipment and lines or rejected as sensible heat in the hot coal and liquid sulfur. The circulating water is kept in balance by returning a portion of the water, stream 32, to the wash section equal to the water vaporized from the feed coal, stream 36.

Neutralization - Sulfate rich wash solution from the wash section, stream 27, is fed to a stirred tank, T-7, and a lime slurry, stream 58, is added to neutralize part of the sulfuric acid. The tank is sized for about 10 minutes of residence time and has a baffled settling zone. Gypsum slurry stream 59 is withdrawn for disposal and the partially neutralized liquid is removed by pump P-19. A portion of the liquid, stream 21, is returned to the reactor section while the remainder, stream 22, is combined with the filtrate, stream 23, as feed to the triple effect evaporators.

Evaporation - Evaporator EV-1 is operated at partial vacuum (about 0.1 atmospheres) and uses condensing steam from the second evaporator, stream 53, to evaporate water, stream 52, in the first evaporator. The evaporated water is condensed in the barometric condenser, B-3, and any residual gas is removed by vacuum pump VP-3. The partially concentrated leach solution, stream 51, is pumped, P-14, to the second evaporator, EV-2. The second evaporator operates at about 155°F and 0.2 atmospheres using steam from the third evaporator, stream 55, to evaporate the water, stream 53. The two condensate streams from the reboilers of the first and second evaporators (streams 53 and 55) are combined, stream 34, to provide clean wash water for the wash section. The leach solution from the second evaporator, stream 54, which has been concentrated to 8.3 percent iron, is at a temperature where the solubility of ferrous sulfate is a maximum and is a solids free solution. This stream is feed to the third evaporator, EV-3, which is operated at atmospheric pressure and at the normal boiling point of the solution. Heat to vaporize water is provided to the reboiler, E-1, by the hot water loop from the wash section (streams 48 and 49). The overhead steam, stream 55, is used in the second evaporator as previously described. The leach solution in EV-3 is concentrated to a total iron concentration of nearly 12 percent which exceeds the solubility of ferrous sulfate. Thus, crystalline ferrous sulfate forms in EV-3 and a portion of the slurry, stream 56, is fed to a centrifuge CG-2 to separate the crystals, stream 57, from the concentrated leach solution, stream 20. The concentrated leach solution is pumped, P-17, to the reactor section.

Solubilities - Since the solubility of ferrous sulfate in the presence of ferric sulfate, sulfuric acid and trace ions is not yet fully defined, the baseline process flows may require some adjustment when pilot scale data have been evaluated. Nevertheless, the planned mode of operation which takes advantage of the reported solubility characteristics of ferrous sulfate in aqueous solution should be applicable. Below about 150°F, the equilibrium crystalline phase is $FeSO_4 \cdot 7H_2O$ which has an increasing solubility with temperature. It reaches a maximum solubility of nearly 60 grams of $FeSO_4$ (anhydrous basis) per 100 grams of water. Above about 150°F the equilibrium solid phase is $FeSO_4 \cdot H_2O$ which has a decreasing solubility in water with increasing temperature. Both the first and second stages of evaporation are below the saturation limits and are expected to remain solids free. Only the final stage operates as a crystallizer and produces crystalline ferrous sulfate both from a decreased solubility at the higher temperature and from an increased concentration because of evaporation.

5.1.2.2 Process Cost Estimate

Throughout bench-scale development, process costs have frequently been reviewed with an objective of focusing experimental effort in the areas of greatest cost sensitivity. The capital cost of equipment required to perform the pyrite leaching must be carefully controlled to maintain a low processing cost per ton of coal product. As will be seen in the capital estimate presented in the following discussion, the major capital cost continues to be in the reactor section of the process. This section of the unit accounts for approximately 48 percent of the total installed equipment capital cost. The sulfur removal section of the process accounts for 22 percent while the wash section represents 17 percent and the sulfate removal section 13 percent of the total equipment capital requirements. It therefore becomes apparent that the reactor section of the process represents the most likely area of future process economic gains as the design data base broadens and other innovative process schemes (relative to the reaction section of the process) are evaluated.

As the process development progressed and additional experimental data were obtained, some complications were identified and some process simplifications were demonstrated. The net result is that at the conclusion of this bench-scale effort, the process for removing pyritic sulfur from coal remains highly attractive and sufficient data has been obtained to provide confidence in the economic viability of the process.

Baseline Capital Cost Estimate - The previous section of this report presented a conceptual process design and process flow sheet for removing 95 percent of the pyritic sulfur from a high ash coal which initially contained 3.2 percent pyritic sulfur. The major equipment for the process is given in Table 26 and identified with the equipment of the flow sheet (Figure 24). The equipment was selected and sized to approach the optimum cost for processing this high pyrite coal to the 95 percent removal level.

TABLE 26. COAL DESULFURIZATION PROCESS EQUIPMENT LIST

REACTOR SECTION $3.26 MM FOB, $6.36 MM INSTALLED*

1	A-1	Ground Coal Feed Hopper - 5000 ft^3
2	C-1	Feed Conveyor - 20 in. Wide x 20 ft, 5 hp, 200 ft/min.
3	K-1	Oxygen Recycle Compressor - 300 hp, 1.6 Compression Ratio
4	M-1A/C	Mix Tank Mixers (3) - 15 hp, Stainless Steel (SS)
5	M-2A/E	Primary Reactor Mixers (5) - 200 hp, SS
6	P-1	Slurry Feed Pump - 1000 gpm, 60 psi, 50 hp, SS
7	P-2	Reactor Discharge Pump - 875 gpm, 5 psi, 3.5 hp, SS
8	P-22A/J	Circulation Pumps (12) - 1000 gpm, 5 psi, 4.0 hp, SS
9	R-1	Primary Reactor - 26 ft Ø x 125 ft, Carbon Steel (CS) with SS clad, 30 psig
10	R-2	Secondary Reactor (3) - 28 ft Ø x 165 ft, SS, 0 psig
11	RV-1	Rotary Valve - .5 hp, 18 in. x 18 in., 20 RPM
12	SP-1	Scrubber-Mist Eliminator - 3 ft Ø x 10 ft, SS, 0 psig, Baffles, Demister Pad
13	T-1	Mix Tank - 18 ft Ø x 36 ft, SS, 0 psig
14	T-2	Flash Drum - 5 ft Ø x 10 ft, SS, 5 psig
15	V-1	Knock-Out Drum - 5 ft Ø x 25 ft, SS, 30 psig, 15 ft Packing, Demister Pad

---

*Installed costs for each process section were derived through the application of the appropriate Guthrie factor[6] to the FOB cost of individual pieces of equipment.

TABLE 26. (CONTINUED)

WASH SECTION $1.16 MM FOB, 2.28 MM INSTALLED

1	B-1	Barometric Condenser - SS, Condensation Rate = 13 Ton/Hr
2	B-2	Barometric Condenser - SS, Condensation Rate = 2.5 Ton/Hr
3	CG-1	Centrifuge (4) - 36 in. Ø x 90 in. Solid Bowl, SS, 150 hp
4	F-1	Rotary Vacuum Filter - 12 ft Ø x 24 ft Drum, 912 ft^2, SS, 8 hp
5	F-2	Rotary Vacuum Filter - 12 ft Ø x 24 ft Drum, 912 ft^2, SS, 8 hp
6	M-4	Contactor Mixer, 35 hp, SS
7	M-5	Contactor Mixer, 35 hp, SS
8	P-3	Contactor Slurry Pump - 1065 gpm, 15 psi, 15 hp, SS
9	P-4	Contactor Slurry Pump - 950 gpm, 15 psi, 10 hp, SS
10	P-5	Leach Filtrate Pump - 450 gpm, 10 psi, 3.5 hp, SS
11	P-6	Leach Wash Water Pump - 560 gpm, 5 psi, 2.5 hp, SS
12	P-7	Filtrate Pump - 590 gpm, 10 psi, 5 hp, SS
13	P-8	Wash Water Pump - 560 gpm, 5 psi, 2.5 hp, SS
14	P-9	Centrate Pump (4) - 150 gpm, 10 psi, 1 hp, SS
15	P-10	Cooling Water Return Pump - 1200 gpm, 5 psi, 5 hp
16	P-11	Cooling Water Return Pump - 200 gpm, 5 psi, 1 hp, CS
17	T-3	Contactor - 40,000 gal, 0 psig, SS
18	T-4	Contactor - 40,000 gal, 0 psig, SS
19	T-5	Centrate Receiver (4) - 650 gal, 0 psig, SS
20	V-2	Filtrate Receiver - 2,000 gal, Vac, SS
21	V-3	Wash Receiver - 2,500 gal, Vac, SS
22	V-4	Filtrate Receiver - 2,500 gal, Vac, SS
23	V-5	Wash Receiver - 2,500 gal, Vac, SS
24	VP-1	Vacuum Pump - 3000 SCFM, 200 hp, CS
25	VP-2	Vacuum Pump - 3000 SCFM, 200 hp, CS

TABLE 26. (CONTINUED)

SULFUR REMOVAL SECTION $1.42 MM FOB, $2.94 MM INSTALLED

1	C-1	Gas Cooler - 7 ft Ø x 100 ft, Water Sprays, SS, 15 psig
2	D-1	Flash Dryer - 11 ft Ø x 65 ft Drying Section, 22 ft Ø x 20 ft De-entrainment Section, SS, 20 psig
3	H-1	Recycle Gas Heater - 97 MM Btu/Hr, Radiant Section = 6000 ft^2, Convective Section = 12,000 ft^2, SS Tubes
4	K-3	Compressor (2) - 1.15 Compression Ratio, 3500 hp
5	P-12	Process Water Pump - 4850 gpm, 40 psi, 150 hp, CS
6	P-13	Sulfur Pump - 3 gpm, 25 psi, 0.5 hp, SS
7	S-1	Cyclone Separator - SS, 15 psig, 120,000 ACFM Capacity
8	S-2	Cyclone Separator - SS, 15 psig, 107,000 ACFM Capacity
9	S-3	Phase Separator - 50,000 gal, 15 psig, SS
10	SC-1	Screw Conveyor - 20 ft x 14 in. Ø, 2 hp, SS
11	SC-2	Pressure Let Down Screw Conveyor - 20 ft x 14 in. Ø, 2 hp, CS
12	SC-3	Coal Cooler - Screw Type, 20 ft x 14 in. Ø, Cooled Shell, CS, 2 hp

TABLE 2C. (CONTINUED)

SULFATE REMOVAL SECTION $0.97 MM FOB, $1.68 MM INSTALLED

1	B-3	Barometric Condenser - SS, Condensation Rate = 35.4 Ton/Hr
2	CG-2	Sulfate Crystal Centrifuge - 36 in. Ø x 72 in. Solid Bowl, SS, 125 hp
3	E-1	Concentrate Recycle Reboiler - 10,000 ft^2, SS/SS
4	EV-1	First Stage Evaporator - Evaporation Rate = 35 Ton/Hr, 1.5 psia, SS
5	EV-2	Second Stage Evaporator - Evaporation Rate = 35 Ton/Hr, 3.7 psia, SS
6	EV-3	Third Stage Evaporator - Evaporation Rate = 38 Ton/Hr, 13 psia, SS
7	M-6	Neutralizer Mixer - 5 hp, SS
8	P-14	Evaporator Concentrate Pump - 520 gpm, 5 psi, 2.0 hp, SS
9	P-15	Evaporator Concentrate Pump - 380 gpm, 5 psi, 1.5 hp, SS
10	P-16	Evaporator Concentrate Pump - 1380 gpm, 5 psi, 5.0 hp, SS
11	P-17	Leach Solution Return Pump - 220 gpm, 30 psi, 5.0 hp, SS
12	P-18	Cooling Water Return Pump - 8000 gpm, 5 psi, 30 hp, CS
13	P-19	Leach Solution Return Pump - 560 gpm, 30 psi, 10 hp, SS
14	P-20	Calcium Sulfate Slurry Pump - 3 gpm, 5 psi, 0.5 hp, SS
15	T-6	Centrate Receiver - 900 gal, SS, 0 psig
16	T-7	Neutralizer Tank - 7,500 gal, SS, 0 psig
17	VP-3	Vacuum Pump - 700 CFM, 50 hp

TOTAL ESTIMATED CAPITAL - $6.81MM FOB, $13.26MM INSTALLED

Capital equipment costs were obtained from various sources: technical literature, equipment suppliers and internal (TRW) costing data. The specific sources of data for the various classes of equipment are presented in Table 27 . When cost data were obtained from literature or other non-current sources, appropriate cost escalation factors, based on the Marshall and Swift Equipment Cost Index (to escalate costs from date of publication to June 1975), were applied. The capital equipment cost for each processing section is presented in Table 26. The costs are presented in terms of FOB equipment cost and installed equipment cost. The FOB equipment cost is the base, uninstalled cost at point of manufacture or point of shipment. The installed equipment cost includes the following elements:

- FOB Equipment Cost
- Field Materials
  - Equipment
  - Piping
  - Concrete
  - Steel
  - Instruments
  - Electrical
  - Insulation
  - Paint
- Material Erection
- Direct Field Labor
- Indirect Costs
  - Freight
  - Taxes
  - Construction Overhead
  - Fringe Benefits
  - Labor Burden
  - Field Supervision
  - Temporary Facilities
  - Construction Equipment
  - Small Tools
  - Miscellaneous Field Costs
  - Contractor Engineering Costs

The installed equipment cost does not include a contingency factor.

TABLE 27. SOURCES OF EQUIPMENT COST INFORMATION

Equipment Type	Information Source
Hoppers	TRW Data
Conveyors	Reference 7
Compressors	Elliott Company
Mixers	Reference 8
Pumps	Reference 6
Reactors	TRW Data
Vessels >40,000 gal	TRW Data
Vessels <40,000 gal	Reference 6
Tanks >40,000 gal	TRW Data
Tanks <40,000 gal	Reference 6
Drums	Reference 6
Centrifuges and Support Equipment	Bird Machine Company
Filters and Support Equipment	Ametec Company
Heat Exchangers	Reference 6
Evaporators	Reference 9
Gas Cooler	TRW Data
Dryer	TRW Data
Heater	Reference 6
Cyclone Separators	TRW Data
Rotary Valves	Reference 6

Operating Cost Estimate - The process operating costs have also been estimated. The basis for these estimates was technical literature and informal supplier quotes. Specific sources of information are presented in Table 28.

The total estimated processing cost has been determined as follows:

Capital Related Costs:	Annual Cost, $1000
Depreciation - 10% straight line	1,326
Maintenance, insurance, taxes, interest (15% of capital)	1,989
Labor:	
Labor, 8 operating positions	1,200
Utilities:	
Electrical power - 7500 KW (25 mil/Kw-hr)	1,500
Cooling water - 20°F rise; 9500 gpm (5¢/1000 gal)	228
Heating - 97 MM Btu/hr; coal, 4T/hr	-
Process water - 110 gpm (25¢/1000 gal)	13
Materials:	
Oxygen 99.5%, 3.9T/hr ($25/T)	780
Lime - .5T/hr ($28/T)	112
TOTAL COST	7,148

Processing Cost (100 T/hr; 0.8 MM T/yr) $8.94/T of feed coal

Coal yield (weight basis)	90%
Coal yield (Btu basis)	94%

The added cost of energy may also be considered for the baseline coal. If the baseline coal is similar to the Lower Kittanning coal utilized in our laboratory studies, it will contain about 20 percent ash and have a heating value of 12,300 Btu/lb as fed. After processing the coal will be 89 percent recovered, have 16 percent ash, and have a heating value of 12,900 Btu/lb. With feed coal prices at $15.00/T the feed costs 61¢/MMBtu. After processing the available energy costs $1.04/MMBtu.

Based on the current conceptual process design, it is concluded that a broad spectrum of Eastern coals can be processed at costs of about $9.00 per ton. It was assumed in developing these costs that the pyrite removal plant is coordinated with a power plant which will have the principal

TABLE 28. SOURCES OF OPERATING COST INFORMATION

Cost Element	Information Source
Maintenance, Insurance, Taxes and Interest	Reference 8
Labor Requirement (Number of Positions)	Reference 8
Labor Cost	TRW Data
Utilities	
Electrical Power	Reference 8
Cooling Water	TRW Data
Process Water	Reference 8
Oxygen	Linde, Division of Union Carbide
Lime	Reference 10

off-site facilities such as coal grinding facilities, change house, offices, rail facilities, etc. To the extent that these off-sites are not available or for bookkeeping purposes are prorated to the coal processing cost, the direct costs given above will be increased.

5.1.3 Process Trade-Off Studies

At the start of this bench-scale program a conceptual process design was available based on data generated in the previous program.[1] Early bench-scale experiments showed that in the elemental sulfur recovery section, the desired displacement of the aqueous leach solution by an organic sulfur solvent could not be reliably performed. Similarily, displacement of the organic solvent by wash water did not occur. The demonstrated fall-back process using parafinic or aromatic hydrocarbon solvents as used in the current bench-scale effort is thought to be less attractive at a commercial scale than sulfur vaporization for three main reasons:

- Higher equipment capital cost for the multiple extraction, solvent distillation and sulfur crystallization.

- Higher energy use, estimated at 4 to 5 percent of the coal, because the heat is rejected at too low a temperature level to be used in the sulfate removal section.

- Loss of solvent on the coal (less than 1 percent and probably only a few tenths of a percent).

Therefore, the more favorable alternate shown in the baseline design (Section 5.1.2) was developed and demonstrated to be operable by laboratory experiments.

With the coal washing and sulfur removal process identified, emphasis centered on the reactor section cost. It was pointed out in Section 5.1.2.2 that nearly one-half of the process equipment cost is associated with the reactor section in the baseline design. Consequently, the majority of the trade-off studies conducted during the course of the experimental phase of the program and the more concentrated effort performed during the subsequent conceptual process design were concentrated on the reaction section. A number of the more pertinent results are summarized in the following paragraphs.

5.1.3.1 Reactor Model

Bench-scale results showed the initial rate of pyrite reaction increased with increased temperature (and pressure). This increased rate only applied to removal of the first 70 or 80 percent of the pyrite after which the rate at high temperature was about the same as the rate obtained at the normal boiling point of the leach solution. A computer model was prepared describing the reaction in a continuous well stirred reactor. Since the coal particles have a statistical distribution of residence times ranging from zero to infinity, some particles have very little removal while others with long residence time have very high removals. The coal was grouped into a variable number of equal weight fractions and reacted for average residence time calculated as the arithematic mean time for the group. For ten time groups the numerical error in pyrite removal compared with the integrated results was about one percent, the error was negligible with 100 or 1000 groups. When this computer routine was incorporated into the overall reactor computer model, forty time groups were selected to provide results with virtually no numeric error.

In a multistage reactor, coal from the first well stirred stage continuously enters the next stage. Thus, if it is assumed that the first stage is fed with a coal of uniform pyrite concentration, the calculated effluent from the first stage will contain coal with 40 different pyrite concentrations. Since each of these coal fractions reacts at a different rate, the effluent from the second stage would have 40 times 40 different pyrite concentrations. After 3 stages, the 64,000 different pyrite concentrations would exceed the storage capacity of the time sharing computer. It was decided that the feed to a stage could be adequately represented by five groups of coal of different pyrite concentrations. Each coal group was reacted for the 40 time increments to give 200 output pyrite concencentrations would strain the storage capacity of typical time sharing computer systems and a few more stages would exceed the capacity of large computers. It was decided that the feed to a stage, other than the first stage, could be adequately represented by five groups of coal of different pyrite concentrations. Each coal group was reacted for the 40 time increments to give 200 output pyrite concentrations for a reactor stage. These 200 values were sorted and rearranged by increasing pyrite concentration. The average pyrite concentrations for the lowest 40, the next lowest 40, etc. was used to provide the five starting concentrations for the next stage calculation. The numeric error introduced by this procedure was not determined, but is believed to be negligible. Greater error will certainly be caused in a real coal by the inhomogeneity of pyrite concentration in the starting coal particles and variation in particle residence time caused by particle size and density variation. The departure of a real coal from ideal particle behavior assumed in the model would tend to increase the real removal efficiency of a stage by retarding the progress of the larger particles and the more dense high pyrite particles.

5.1.3.2 Pressure Effect

The cost-pressure trade-off was expected to be a critical study in the process design. The overall trade-off is somewhat complex since there are a number of interactions among the streams and equipment that make up the reactor system. A simplified diagram is shown in Figure 25.

Coal and recycled leach solution are fed to a multistage mixer where some pyrite reaction occurs. The leach solution in stream 1 has increased in total iron and decreased in Y (ratio of ferric iron to total iron) as a result of the reaction occurring in the mixer. In the first (primary) reactor the temperature is set at the design value and oxygen is present at the design pressure to oxidize ferrous iron to ferric iron and thereby increase the solution Y. Both the pyrite reaction and the iron oxidation liberate heat. Part of the heat is lost from the reactor walls and part is needed to heat stream 1 from the mixer temperature to the reactor temperature. The balance of the heat is removed to maintain the reactor at the design temperature. This heat is removed by vaporizing water which is condensed outside the reactor by contact with the recycle leach solution. The reactor total pressure is a sum of the steam pressure at the temperature of reaction, the specified oxygen pressure and the partial pressure of inert gas which builds up in the recycle gas loop.

When the reactor oxygen pressure is high, the fraction of steam in the gas is low and high circulation rates are required to remove the steam formed to maintain constant reactor temperature. Thus, high oxygen pressure increases the pressure rating of the reactor and the amount of recycle gas compression, but it increases the rate of reaction by providing a higher Y and thereby decreases the required residence time and reactor size.

The effluent from the primary reactor, stream 2, is fed to the secondary reactor which removes additional pyrite and decreases the Y of the leach solution. If the residence times in the mixer and the primary reactor are preselected in reasonable ranges, then a residence time for the secondary reactor can be found which gives the desired pyrite removal. Figure 26 shows the time trade-offs between the primary reactor, R-1, and the secondary

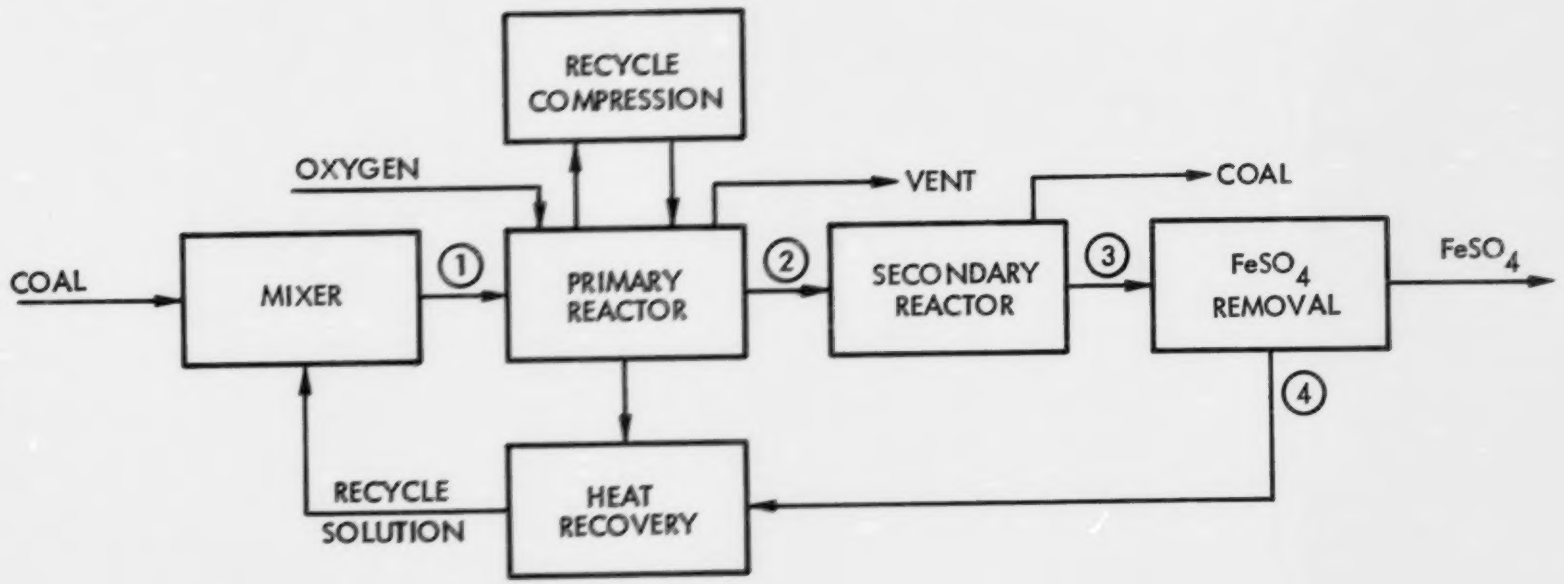

COAL
MIXER
①
OXYGEN
RECYCLE COMPRESSION
PRIMARY REACTOR
VENT
②
SECONDARY REACTOR
COAL
③
$FeSO_4$ REMOVAL
$FeSO_4$
④
HEAT RECOVERY
RECYCLE SOLUTION

Figure 25. Simplified Reactor System

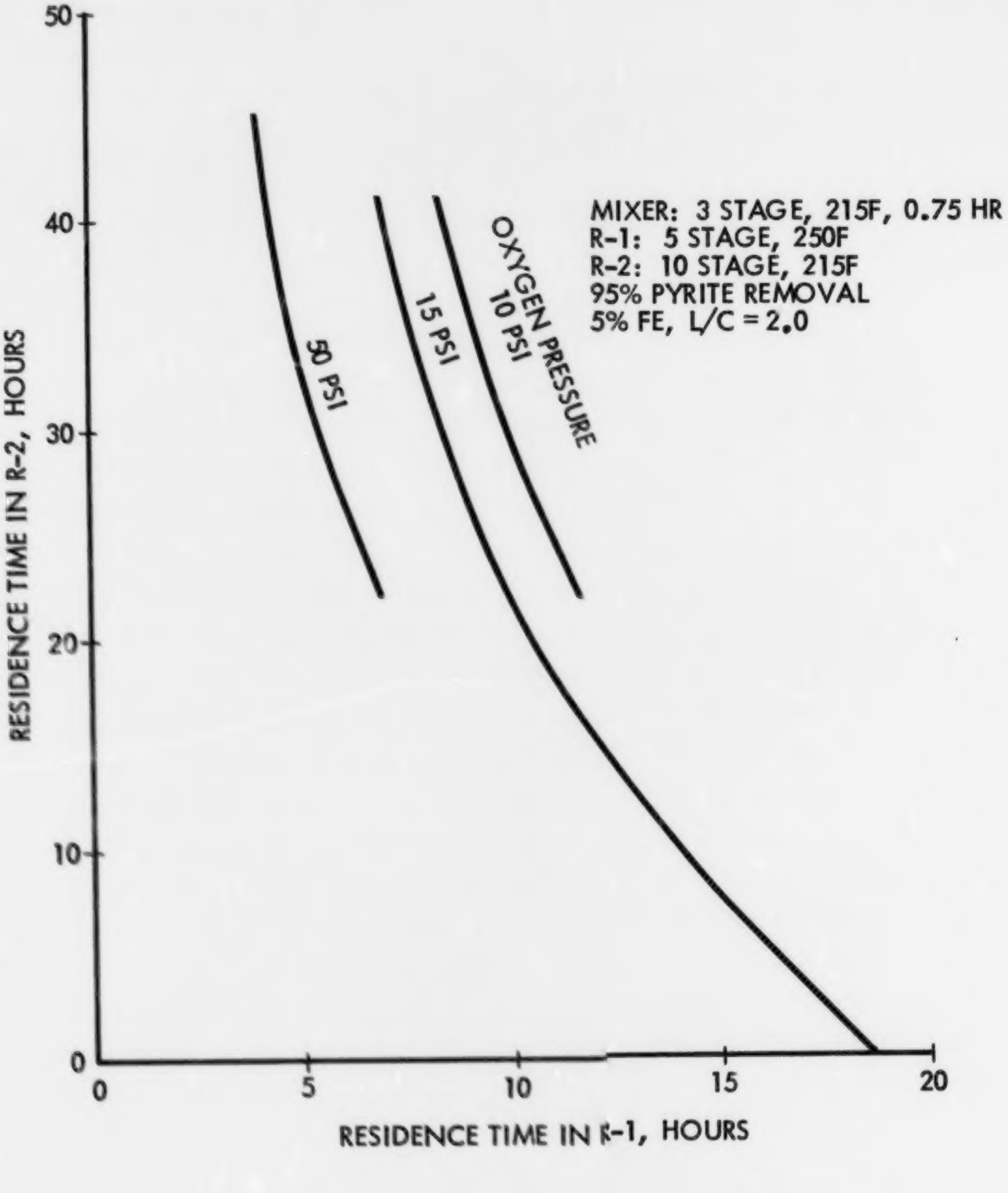


Figure 26. Reactor Residence Times as a Function of Oxygen Pressure in R-1

reactor, R-2, at three oxygen pressures. A primary reactor is always required to regenerate the leach solution since there is not sufficient ferric iron to react with the desired pyrite. In principal it is possible to avoid a secondary reactor if sufficient time is provided in the primary reactor. For example, the figure shows that at 15 psi oxygen pressure, 18.8 hours of reaction time in the primary reactor will remove 95 percent of the pyrite without a secondary reactor.

Pyrite removal is not the only criteria for selecting pressure and residence times. It is also necessary to remove the iron sulfate formed from the pyrite reaction. The baseline design removes as ferrous sulfate all of the iron formed in the pyrite leaching reaction. Therefore, the reactor effluent must contain enough iron in the ferrous form (low enough Y) to provide this quantity of ferrous iron. Referring again to the simplified reactor system diagram, if the secondary reactor effluent, stream 3, has a Y of 0.67, then removal of the ferrous sulfate from reaction will increase the Y to 0.85 for recycle. Returning a recycle solution with a Y higher than about 0.85 presents problems in crystallizing the ferrous sulfate from a solution which is too rich in ferric sulfate. Figure 27 shows the influence of residence time in the secondary reactor on the effluent ferrous iron. Instead of presenting the data in terms of Y, the figure gives the available ferrous iron per 100 moles of pyrite fed based on a recycle Y of 0.85. Thus, if the coal has 95 percent pyrite removal, 95 moles of ferrous iron must be available. It is evident that secondary reactor residence times in the vicinity of 35 to 40 hours are needed to provide this quantity of ferrous iron.

To find the effect of pressure, computer runs were made at the correct residence time for 95 percent removal with 95 moles of available ferrous iron at pressures from 10 to 50 psi. The results are as follows:

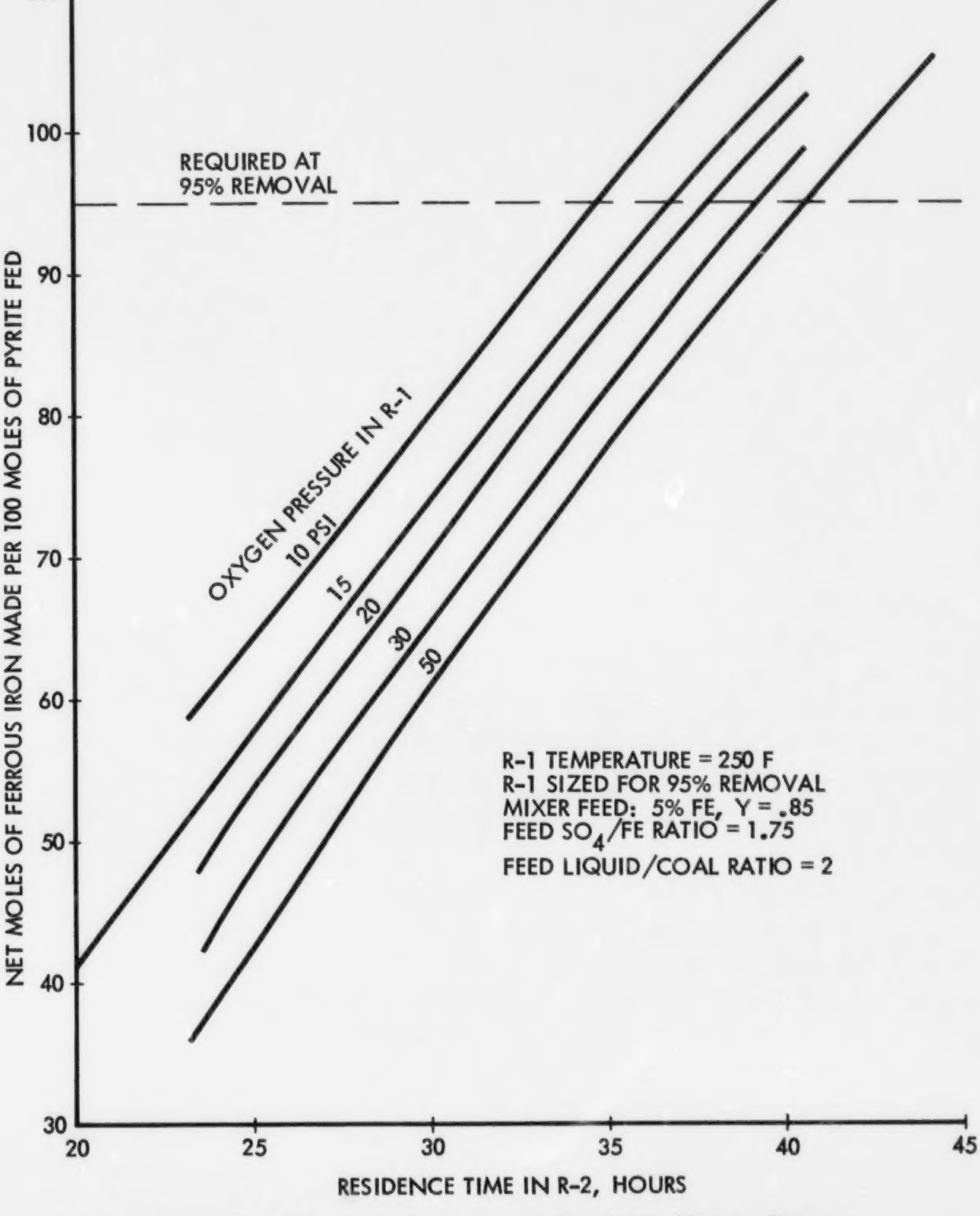


Figure 27. Effect of Pressure and Residence Time on Ferrous Iron Make

O_2 Pressure psi	Residence Times R-1, hr	R-2, hr	Reactor System Cost* $000
10	9.21	34.8	2835
15	7.39	36.7	2814
20	6.40	37.9	2824
30	5.30	39.3	2858
50	4.27	40.7	2938

---

*Includes: Mixer, R-1, R-2, Knockout drum and recycle compressor.

These results are presented in Figure 28 which shows that most of the cost is in the primary and secondary reactors. It may be seen that the cost minimum is very broad. Although minimum cost is near 15 psi of oxygen, it was concluded that any pressure in this range can be used if it was found to be more desirable for other reasons.

5.1.3.3 Iron Concentration Effect

The baseline process has a leach solution containing 5 weight percent iron in the mixer feed. After pyrite leaching and water evaporation the iron concentration increases to 6.7 percent. Likewise the feed ratio of sulfate to iron is 1.75 which decreases to 1.64 at the secondary reactor effluent. Calculations were also performed with a mixer feed of 4 percent which gave an effluent iron level of 5.6 percent. The comparative cost results are as follows (for 15 psi oxygen pressure):

	5% iron feed	4% iron feed
Mixer, 3 stage	0.75 hour	0.75 hour
R-1, 5 stage	7.39 hour	8.91 hour
R-2, 10 stage	36.7 hour	38.2 hour
Equipment cost (FOB)		
Mixer	$118,000	$120,000
R-1	896,000	1,074,000
R-2	1,708,000	1,804,000
R-1 Knockout	28,000	28,000
Compressor	64,000	65,000
Total	$2,814,000	$3,091,000

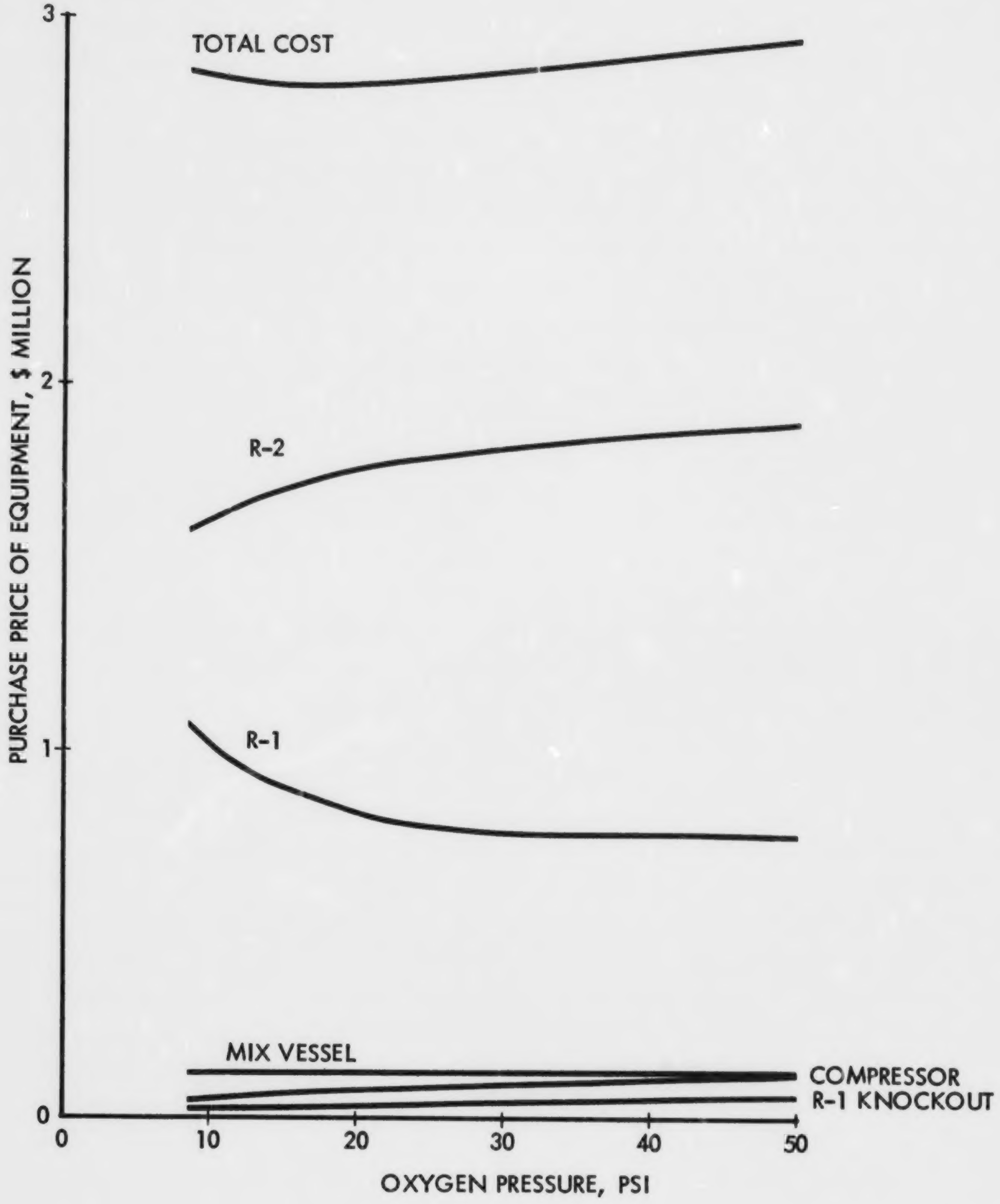


Figure 28. Reactor System Cost as a Function of Oxygen Pressure

The purchased equipment cost increase in the reactor section resulting from a decrease of 1 percent in iron concentration is seen to be $277,000 or nearly 10 percent. Cost impact on downstream portions of the process were qualitatively examined. A negligible cost impact on equipment in the sulfate and sulfur removal sections was found, although about 10 percent less wash water would be required to remove the aqueous sulfate leach solution. The evaporators with a cost of about $0.5 million could be reduced in size to produce less wash water, but the overall cost reduction would appear to be not more than $50,000. It was concluded that total downstream process equipment cost reduction will be much less than the $277,000 increase in reactor cost. Therefore reducing iron concentration will result in a small increase in process equipment cost.

5.1.3.4 Oxygen Purity

The evaluation of the effects of oxygen purity includes the effects of inert gas concentration in the purchased oxygen and the effects of inert gas buildup in the recycle stream, but ignores any inert gas that may be generated from the coal during leaching. A simple diagram of the oxygen system is shown in Figure 29. At steady state the recycle flow rate is set by the requirement to remove steam from the reactor for temperature control as described in Section 5.1.3.2. Also at steady state, the flow rate of oxygen in the feed must equal the rate of oxygen consumption plus the flow rate of oxygen in the vent stream and the quantity of inert gas vented must equal the quantity of inert gas in the oxygen feed. The oxygen vented (wasted) depends on its concentration in the vent stream and therefore its partial pressure in the reactor. For a given coal and reactor temperature and oxygen pressure, the oxygen concentration in the vent stream depends on the inert gas buildup in the reactor. The larger the buildup of inerts in the reactor the lower will be the oxygen waste through the vent. However, since the reactor temperature and oxygen pressure are fixed, the higher the inert gas buildup the higher the total pressure and thus the reactor pressure rating requirement. Obviously there is a tradeoff to be made between the cost of oxygen wasted an- the cost of the reactor. For the purpose of comparing the operating cost of purchased oxygen with the capital cost of the reactor, the following criteria, based on cost data in Section 5.1.2.2, were applied:

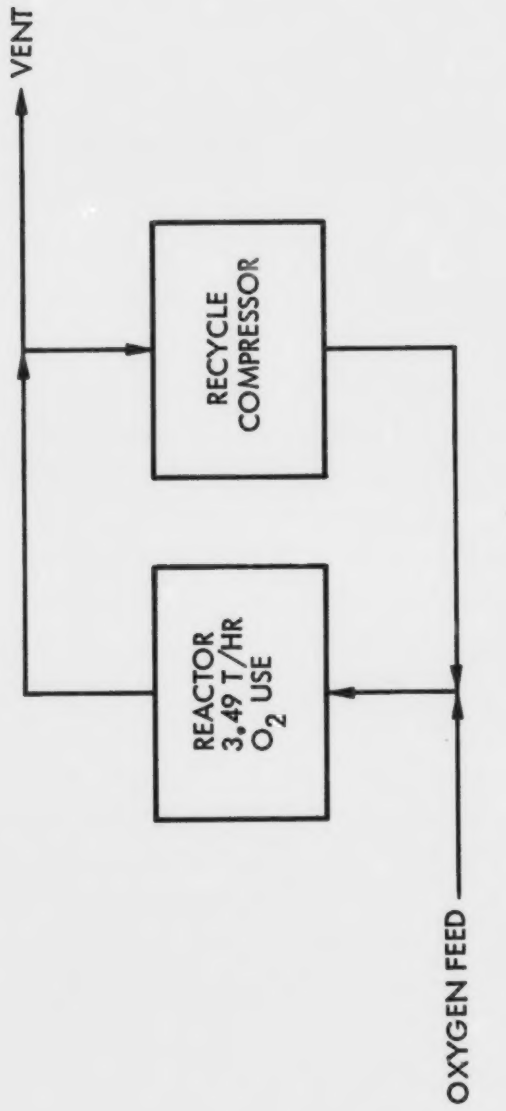

VENT
RECYCLE COMPRESSOR
REACTOR
3.49 T/HR
O_2 USE
OXYGEN FEED

Figure 29. Oxygen Circulation Diagram

- Oxygen at 99.5 percent purity by gas volume up to 300 psi is priced at $25/T.

- Annual cost of capital is a total of 25 percent which included depreciation, maintenance, insurance, taxes and interest.

- The capital for installed reactor equipment is twice the purchase price; the actual ratio for the baseline case is 6.36/3.26 = 1.95.

Table 29 shows the influence of oxygen purity both in the reactor gas and in the purchased gas on the cost variable components of the reactor system. For comparison, purchased purities of 99.5 percent and 95 percent were selected. The 95 percent pure oxygen is usually priced lower (based on contained oxygen) because the argon/oxygen separation step is not required. At a price of $20/ton of contained oxygen for 95 percent purity, the comparison shows that slightly lower cost can be obtained with the lesser purity oxygen gas if the lower purity oxygen is recycled to about 50 percent consumption. The difference, which is only $50,000/yr (about $.06/ton of coal), disappears if the differential in oxygen is actually $3/T of contained oxygen instead of the $5/T used in Table 29. When high purity oxygen is used recycle ratios can be set to give inert gas buildup in the range of 5 to 50 percent inert gas in the reactor at little change in process cost. With 95 percent oxygen the range is about 15 to 70 percent inert gas in the reactor. The baseline case was chosen at 5 percent inert gas in the reactor using 99.5 percent oxygen feed to allow for any coal derived inert gas generation during the leaching operation.

5.1.3.5 Compressed Air Regeneration

The cost of oxygen has increased two or three fold in the last five years and it is necessary to reexamine the substitution of compressed air for oxygen. Compressed air could be of interest if its cost in the Meyers Process were less than oxygen or if it is similar in cost but significantly reduces the energy consumption of the process.

TABLE 29. EFFECT OF INERT GAS BUILDUP ON REACTOR SECTION ANNUAL COST

Oxygen Gas Containing 0.5% Inert (\$25/T of O_2)

Reactor inert gas, %	2	5	10	20	50	80	90
Reactor pressure, psig	53	54	55	57	68	113	163
Oxygen vented, T/hr	1.14	.37	.17	.07	.02	.00	.00
Equipment cost, \$000 (FOB)							
R-1	901	905	913	931	1031	1429	2087
R-1 knockout	28	28	29	31	40	56	111
Compressor	60	64	67	72	90	123	142
Total	989	997	1009	1034	1161	1608	2340
Annual cost, \$000*							
Capital related	494	498	504	517	580	804	1170
Total O_2 cost	913	760	712	701	691	687	687
Total cost, \$000	1407	1258	1225	1218	1271	1491	1857

Oxygen Gas Containing 5% Inert (\$20/T of O_2)

Reactor inert gas, %	7	10	15	20	50	80	90
Reactor pressure, psig	54	55	56	57	68	113	163
Oxygen vented, T/hr	8.13	3.15	1.49	.93	.19	.04	.00
Equipment cost, \$000 (FOB)							
R-1	908	913	922	931	1031	1429	2087
R-1 knockout	27	29	30	31	40	56	111
Compressor	29	54	63	68	89	123	142
Total	964	996	1015	1030	1160	1608	1857
Annual cost, \$000*							
Capital related	482	498	508	515	580	804	1170
Total O_2 cost	1838	1049	786	697	580	553	550
Total cost, \$000	2320	1547	1294	1212	1160	1357	1720

---

*Power cost for the recycle compression was neglected because it was too small to affect the cost comparison.

The reactor section was sized and costed in a manner similar to the method used for examining oxygen purity (Section 5.1.3.4). A summary of the results is shown in Table 30. Three oxygen partial pressures were included, namely: 15, 10 and 5 psi and for each oxygen partial pressure three levels of oxygen utilization were examined. It had been the plan to examine 75, 50 and 25 percent use of the oxygen, but convergence logic in the computer model sometimes prevented the 25 percent point from being obtained. Basically the problem relates to water balancing the reactor system.

It is evident from the results that the major trade-off occurs between reactor cost and compression cost. For example, at 15 psi of oxygen partial pressure when the oxygen is 75 percent consumed, the reactor pressure needed is 338 psig largely from the high concentration of nitrogen in the reactor vent gas. If the oxygen in the air is only 25 percent used the reactor pressure decreases to 138 psig. However, while the reactor cost decreases with decreasing pressure, the compression cost increases and the optimum at 15 psi of oxygen pressure is between these extremes.

A second factor is water vapor loss from the reactor. The reactor operating at 250°F and sized for an overall removal of 95 percent of the pyrite from a 3.2 percent pyritic sulfur coal produces excess heat equivalent to about 12 tons per hour of water vaporized in the reactor. As either the oxygen partial pressure decreases or the percent oxygen utilization decreases the water vapor in the vent gas increases. Thus at 15 psi oxygen pressure oxygen utilization can be decreased to less than 25 percent before all excess steam is removed, but at 5 psi of oxygen pressure something less than 45 percent (probably 35 to 40%) is the lowest utilization possible. If the reactor temperature is increased above 250°F or a coal with less starting pyrite is used, even greater oxygen utilization than shown in Table 30 will be required.

The cost comparison shown in Table 30 was made on the assumption that the large quantity of pressurized vent gas can provide one-half of the energy needed to compress the feed air. Even with this optimistic assumption, it may be seen that the process costs are higher with air than the baseline

TABLE 30. EFFECT OF COMPRESSED AIR ON REACTOR SECTION ANNUAL COST

	Baseline 99.5% O_2	Regeneration with Compressed Air								
Oxygen pressure, psi	15	15	15	15	10	10	10	5	5	5
Reactor pressure, psig	54	338	188	138	238	138	109	138	88	83
Oxygen used, % of feed	90	75	50	25	75	50	30	75	50	45
Water vented, T/hr	.0	.2	.7	3.1	.4	1.1	4.1	.7	2.4	3.5
Recycle compressor, HP	315	880	685	310	810	550	200	625	230	125
Air compressor, HP	-	3235	4095	6600	3235	3485	4880	2455	2730	2910
Equipment cost, $000 (FOB)										
R-1	905	3405	2087	1648	3064	1988	1680	2909	2096	2022
R-1 Knockout	28	242	109	70	149	73	48	75	55	50
Recycle compressor	64	146	120	64	137	100	44	111	50	30
Air compressor	-	414	501	733	414	440	576	333	362	381
Total	997	4207	2817	2515	3764	2601	2348	3428	2563	2483
Annual cost, $000										
Capital related	498	2104	1409	1253	1882	1301	1174	1714	1282	1242
Total O_2 cost	760	-	-	-	-	-	-	-	-	-
Compressor power*	63	500	546	722	486	459	528	371	319	316
	1321	2604	1955	1975	2368	1760	1702	2085	1601	1558

---

*Power cost assumes $0.025/kw-hr and that 50 percent of air compression power is recovered by expanding the vent gas through a turbine drive on the compressor.

process with oxygen. The factor of overall power use also shows that air generally is a significantly higher power consumer. Oxygen is produced at a total energy consumption of about 345 Kw-hr per ton of oxygen. This is equivalent to nearly 1800 horsepower for the oxygen needed in the baseline case. Thus, the baseline which uses a total of about 2100 horsepower for oxygen production and gas recycle is well below any of the air fed cases and only the low pressure, low oxygen utilization case is competitive if the optimistic recovery of energy from the vent gas is assumed. Since no process testing has been conducted at these low oxygen pressure, high gas throughput rates, it is entirely possible that solution foaming may occur or that much greater reactor volumes or residence times may be needed. The current analysis tends to show that oxygen continues to be much preferred over compressed air in the process design.

5.1.3.6 Three Reactor Configuration

In the early stages of the process design, trade-offs were made between the baseline design and a three reactor configuration. The concept of the three reactor configuration was that the first reactor (R-1A) would use oxygen at the highest pressure in a once-through mode to give partial reaction and partial regeneration. The second reactor (R-1B) would continue the reaction and regeneration using the vent oxygen at a lower pressure and lower reactor temperature also in the once-through mode. The third reactor (R-2) would be like the second reactor of the baseline process. Although all of the process constraints were not known in the early cost trade-off studies, the trend was for the first reactor of the three reactor configuration to move toward low pressure and the second reactor to move toward atmospheric pressure and thus become the two reactor (baseline) configuration. Upon completion of the baseline definition a brief examination was made of the cost of a three reactor configuration meeting the processing constraints (pyrite removal and adequate ferrous sulfate in the effluent). Table 31 shows three cases which meet these constraints. It can be seen that in each case the equipment cost is higher than the baseline case. A full study which is both costly and time consuming was not undertaken since it appeared unlikely that there is a configuration with a significantly lower cost than the baseline case.

TABLE 31. EQUIPMENT COSTS FOR A THREE-REACTOR CONFIGURATION

Operating Conditions

	R-1A	R-1B
Baseline	7.49 hrs, 250°F, 15 psi O_2	None
Case 1	2.50 hrs, 250°F, 50 psi O_2	10 hrs, 220°F, 10 psi O_2
Case 2	2.25 hrs, 250°F, 50 psi O_2	14 hrs, 220°F, 5 psi O_2
Case 3	2.00 hrs, 250°F, 50 psi O_2	14 hrs, 225°F, 5 psi O_2

Equipment Cost, $000 (FOB)

	Baseline	Case 1	Case 2	Case 3
Mixer	118	118	118	118
R-1A	905	490	450	409
R-1B	-	825	964	1008
R-2	1677	1677	1677	1677
Knockout	28	-	-	-
Compressor	64	-	-	-
	2792	3110	3209	3212

5.1.3.7 Additional Studies

While the process design effort attempted to examine all of the parameters which were of major importance to providing a low cost process design, it considered only the bench-scale Lower Kittanning coal which had a fairly high level of pyrite and rather poor filtering qualities. As data becomes available on other coals, new designs should be prepared to accommodate other separation rates, different pyrite levels, other levels of pyrite removal, other methods for by-product removal and additional parameters identified during the testing and process design. Since coals may differ significantly in reaction rate and processing parameters, it is likely that several different process flow sheets will be needed to accommodate the heat and mass balances for a wide spectrum of coals. It is likely that the improvements in reaction and filtration rates that appears to come with mechanical precleaning of coal will lead to a still lower cost process.

5.2 COARSE COAL (-1/4 INCH) PROCESSING

The bench-scale efforts relative to the processing of coarse coal (see Section 4) have been principally directed toward the acquisition of data and information on pressurized reaction systems. Comparisons of data for pressurized and unpressurized systems indicate that the imposition of pressure does not significantly influence the pyrite leach rate from coarse coal. Because the use of non-pressurized reaction vessels and support equipment significantly reduces capital investment requirements, a decision was made to formulate a conceptual coarse coal process design on that basis. The rationale, design details and estimated economics of this design are presented in the following subsections.

5.2.1 Concept Development

The physical characteristics and laboratory-derived leach reaction rates of coarse coal required the development of a completely different processing concept than that conceived for fine (suspendable) coal. It is, of course, understood that one of the primary virtues of coarse coal processing is that the product is shippable, handleable and storable by conventional means. In terms of processing, coarse coal usage implies less pre-leaching preparation, the elimination of requirements for product pelletizing or briquetting operations and the potential application of conventional physical separation systems to augment the productivity/investment ratio of the Meyers Process.

The major physical characteristic of coarse coal which necessitates modification of the fine coal processing concept is the tendency of the 1/4" x 0 coal grind to separate. The fines (approximately 48 mesh x 0) are nominally slurryable, while the larger mesh fraction (about 1/4" x 48 mesh) settles out quite rapidly. It is therefore impractical to consider slurry transportation of the coal; because of the tendency for the coal and leach or wash liquors to separate it is in fact much more efficient to retain the coal in a fixed position and allow the liquors to pass through the reacting mass (as in a packed bed) and to transport the coal mechanically by means of conveyor systems.

While the basic leaching reaction established during fine coal investigations is fully applicable, the range of particle sizes included in the nominal 1/4" x 0 grind gives rise to a corresponding range of reaction rates; the fines react in basic accordance with the rate constants derived in the fine coal evaluations, but the coarse particles are considerably slower. Since, as indicated earlier, there is little rate constant advantage offered by the use of pressurized reaction vessels, the coarse coal conceptual process must allow for relatively long coal retention periods. The leaching residence time may be shortened by preprocessing the coarse ROM coal through conventional physical cleaning (scalping) which offers a means of segregating a small, extremely pyrite rich and difficult to leach, fraction of coal for direct disposal. Further economic advantages are indicated when the scalped coal is deep cleaned into two fractions, one lean in pyrite that would not require depyritization and one rich in pyrite to serve as feed stream to the Meyers Process. The recombined product would meet the sulfur standards even though only approximately one half of the ROM coal was subjected to the Meyers Process.

A total of four reactor configurations were identified as potentially viable. These include an above-ground batch reactor; a lined pit batch reactor; a continuous countercurrent reactor; and a continuous cocurrent reactor. All of these possibilities were conceived as atmospheric pressure units in which only the leach reaction occurs; because of the relatively easy coarse coal-from-liquid separation, the regeneration reaction can be accomplished in a separate vessel optimized for that purpose.

The four reactor configurations were simulated with computer models and evaluated in detail. It quickly became apparent that the above-ground batch reactor scheme would be the most expensive and complex of the group and it was therefore eliminated from consideration on that basis. It was also found that the continuous countercurrent reactor requires a smaller vessel and a lower leach solution throughput than the cocurrent reactor, therefore the continuous cocurrent reactor scheme was also eliminated.

Both the continuous countercurrent and batch pit reactor schemes were expanded to complete conceptual flow diagrams for further study. The process, as described in the following paragraphs, could incorporate either reactor type and could be preceded by a physical separation train. The conceptual design is presented schematically in Figure 30. A brief description of the conceptual design follows with details of the key elements being presented in subsequent subsections.

Coal is fed to the reactor, stream 1, at a design rate of 100 TPH where it contacts a continuously regenerated stream of leach solution, stream 2, of $Y_{ENTER} = 0.95$. Spent leach solution, containing a portion of the fines fraction from the coal feed is withdrawn from the reactor, stream 3, and blended with the liquid stream 17 recovered from the coal drain. Stream 17 also contains a portion of the fines fed to the reactor via stream 1 which are acquired during the drain and rinse cycle. The weak leach solution-coal slurry is bled, stream 5, at a rate sufficient to maintain the total iron content of 4 percent and to maintain the fines content of the leach solution loop at a maximum of 10 percent. The fines in bleed streams are removed by filtration with the filter cake being conveyed, stream 7, for reinjection into the coal processing sequence at the water wash step. The filtrate is pumped, stream 6, to a unit which converts the major portion of the Fe^{+3} to Fe^{+2} by iron reduction. The Fe^{+2} rich stream is then sent to an evaporator/crystallizer unit, stream 9, which produces the clean water used in the coal wash, stream 12. The ferrous salt is filtered from the crystallizer output, stream 13, and disposed of through liming, stream 14. Residual solution, taken as filtrate, is routed to the regenerator, stream 11, together with the spent leach solution which bypasses the bleed stream diverter, stream 10. Regeneration of the leach solution is accomplished as outlined in Section 5.1.1 relative to fine coal processing; oxygen is supplied, stream 15, to convert the Fe^{+2} ion and sulfuric acid to Fe^{+3} and water. The freshly regenerated leach solution, stream 2, completes the loop through reinjection into the reactor.

The leach solution-wet coal leaving the reactor, stream 4, is drained on a conveyor and spray rinsed with leach solution-contaminated water,

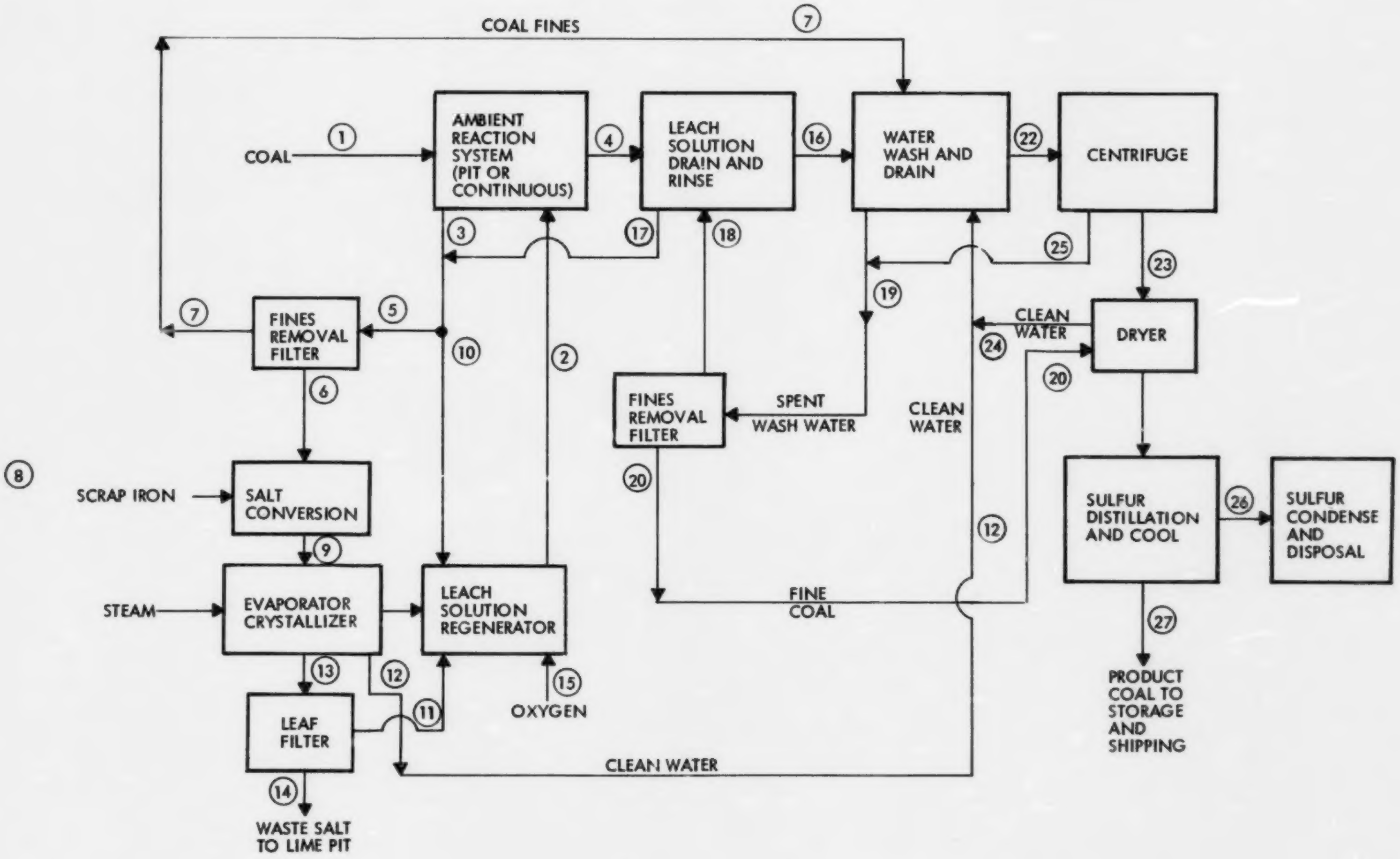

COAL FINES
⑦
COAL
①
AMBIENT REACTION SYSTEM (PIT OR CONTINUOUS)
④
LEACH SOLUTION DRAIN AND RINSE
⑯
WATER WASH AND DRAIN
㉒
CENTRIFUGE
③
⑰
⑱
㉕
㉓
⑲
⑦
FINES REMOVAL FILTER
⑤
⑩
②
CLEAN WATER
㉔
DRYER
⑳
⑥
FINES REMOVAL FILTER
SPENT WASH WATER
CLEAN WATER
⑧
SCRAP IRON
SALT CONVERSION
⑳
⑫
SULFUR DISTILLATION AND COOL
㉖
SULFUR CONDENSE AND DISPOSAL
⑨
STEAM
EVAPORATOR CRYSTALLIZER
LEACH SOLUTION REGENERATOR
FINE COAL
⑬
⑫
㉗
LEAF FILTER
⑪
⑮
OXYGEN
PRODUCT COAL TO STORAGE AND SHIPPING
CLEAN WATER
⑭
WASTE SALT TO LIME PIT

Figure 30. Coarse Coal Process Schematic

stream 18. This rinse water stream is the filtrate obtained by removing fines from stream 19. The wet fines are conveyed directly to the dryer via stream 20.

The wash vessel is sized for a nominal 1-hour residence time to permit transfer of the leach solution trapped in coal pores to the passing water stream, which originates as evaporator and dryer condensates, streams 12 and 24. Following a conveyor draining step similar to that employed earlier to remove excess leach solution, the coal, stream 22, is transported to a continuous centrifuge which reduces the total water content to about 20-22 percent with the centrate, stream 25, going to the fines filter. The coal is conveyed, stream 23, to a two stage inert atmosphere dryer/distillation unit where water is first removed, stream 24, followed by elemental sulfur removal, stream 26. The elemental sulfur is cast into blocks for disposal and the coal, stream 27, is cooled for preshipment storage.

5.2.2 Conceptual Process Details

5.2.2.1 Reactor Section - Pit and Continuous

Both the batch pit and continuous countercurrent reactor concepts were sized to accommodate 100 TPH of 1/4" x 0 ground coal. In the case of the pit reactor, three identical units are required such that filling, leach reaction and raw product coal withdrawal can proceed concurrently; the withdrawal rate, which sizes the balance of the process units, is 100 TPH. The pit reactor configuration, upon which the conceptual process design is based, is shown schematically in Figure 31 . As can be seen, the sectional view indicates a basically triangular pit with the sides angled at 30° such that the natural angle of repose of wet coal is exceeded and the coal can be withdrawn via the conveyor at the bottom. The pit and drain pump lining material is acid-resistant concrete and the metal parts and various exposed equipment items are of stainless-clad mild steel. Each pit is sized to hold sufficient coal for 5 days of operation, i.e., 12000 tons at the 100 TPH withdrawal rate. Using a bulk density of 47 lb/ft^3, the reactor volume is 511,000 cubic feet; for a 300 foot length, the tank width is about 43 feet and the depth about 80 feet.

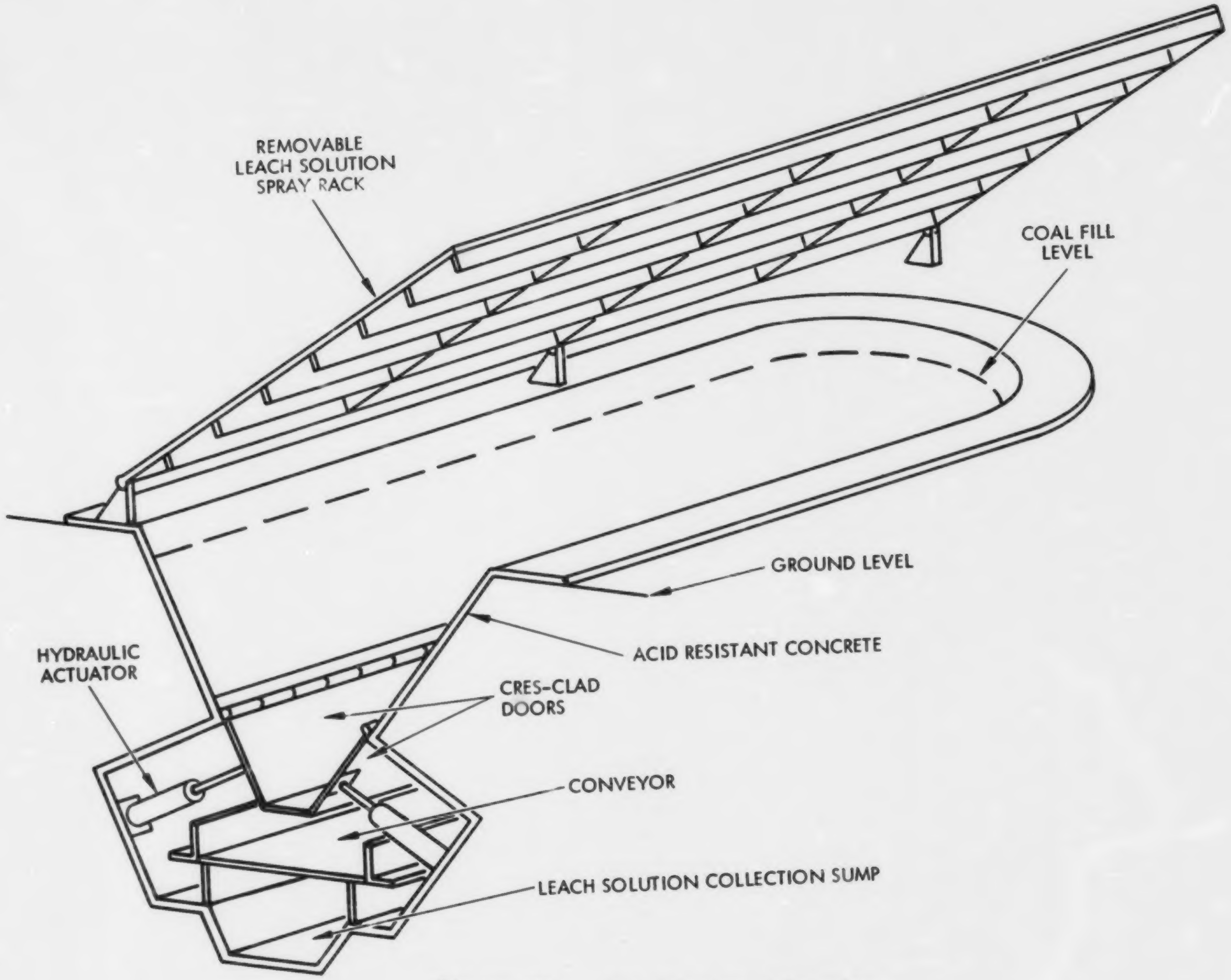

REMOVABLE LEACH SOLUTION SPRAY RACK
COAL FILL LEVEL
GROUND LEVEL
ACID RESISTANT CONCRETE
HYDRAULIC ACTUATOR
CRES-CLAD DOORS
CONVEYOR
LEACH SOLUTION COLLECTION SUMP

Figure 31. Pit Reactor Schematic

The leach solution is distributed over the upper surface of the coal mass by means of a hinged spray rack which can be moved for pit load operations. The leach solution drains through the coal bed, is collected in a full-length sump, and is circulated back to the regenerator. Following completion of the leach reaction, coal is withdrawn from the pit reactor by opening the hydraulically-operated doors comprising the lower one-third of the reactor wall; this allows the coal to fall onto a nominal 48 mesh conveyor and to drain residual leach solution while being transported to the rinse section of the plant.

The five day pit capacity imposes a similar limit on the leach reaction period. Based on bench-scale and laboratory data, rate constants were estimated which show that about three days of leaching will be required to reduce pyrite to target level. The design over-capacity allows for the use of coals having a higher pyrite content or the processing of a pyrite-rich fraction from a front-end physical separation/pyrite concentration unit as described earlier.

All three pit reactors are serviced by a track-mounted reclaim-conveyor system having a 120 TPH capacity; this unit reclaims coal from a pile and distributes it along the length of each pit. The 120 TPH capacity assures maintenance of any operating cycle time within the 5-day maximum imposed by the reactor design.

The ambient-pressure continuous countercurrent reactor system concept was also sized for a 100 TPH feed rate. Each reactor (see Figure 32) consists of a cylindrical outer shell having a conical bottom and a discharge lock hopper at the lower end of the cone. A raised lip surrounds the upper periphery of the cylindrical shell, stainless steel clad is used over all interior surfaces, a spreader cone at the top distributes the feed coal over the cylindrical area and a series of internal baffle plates limits the formation of any flow channels which may develop. The conical bottom section houses the leach solution distribution orifices through which leach solution is forced under pressure to flow upward through the coal bed.

Operationally, coal is loaded at the top of each reactor at the design feed rate and is distributed by the spreader plate; continuous withdrawal

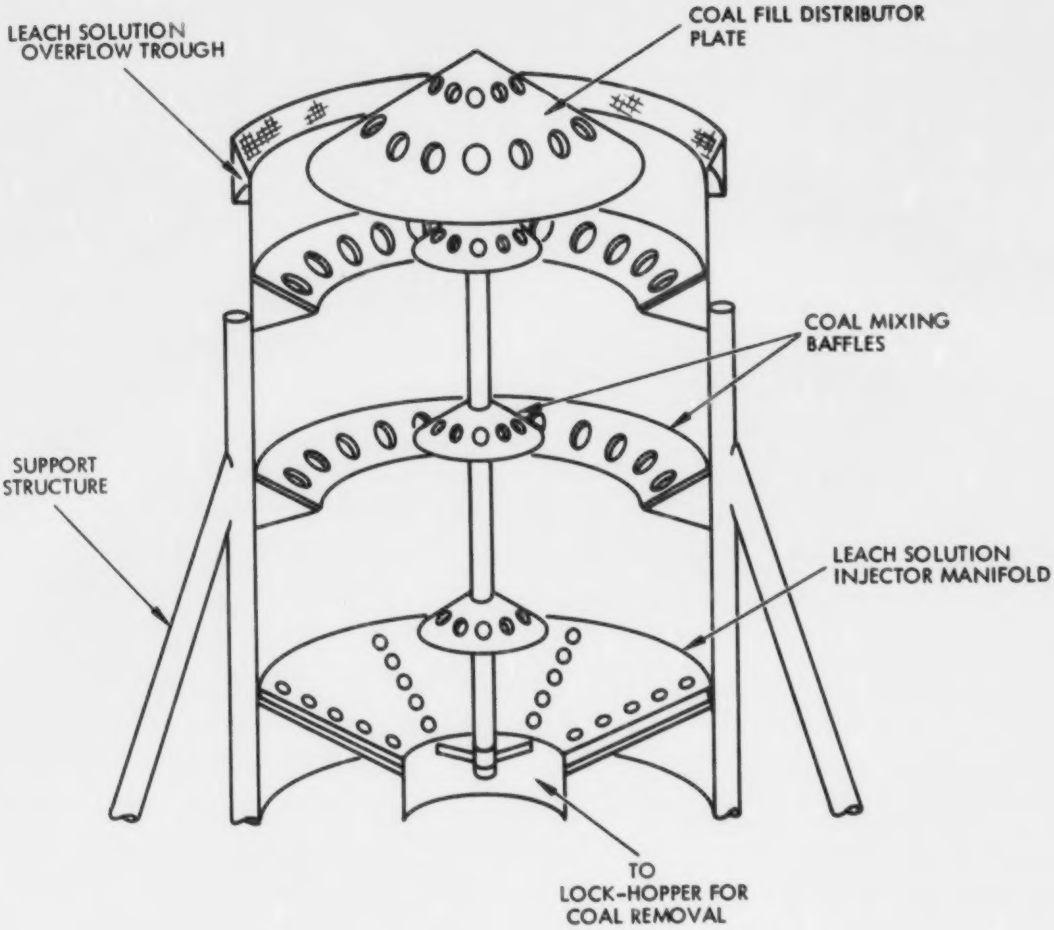

LEACH SOLUTION OVERFLOW TROUGH
COAL FILL DISTRIBUTOR PLATE
COAL MIXING BAFFLES
SUPPORT STRUCTURE
LEACH SOLUTION INJECTOR MANIFOLD
TO LOCK-HOPPER FOR COAL REMOVAL

Figure 32. Continuous Reactor Schematic

through the base lock hopper provides a nominally uniform downward travel of the coal. The design residence time for processing feed coal having a 3.2 percent pyritic sulfur content is 50 hours. The reactor system consists of five vessels each 20 feet in diameter and holding 1000 tons of coal. With feed and withdrawal rates of 20 TPH, coal leaching occurs in about 80 feet of vessel length. Leach solution at a rate of 286 TPH flows upward through the coal at a rate of less than 0.01 ft/sec. The feed leach solution has a Y of 0.95 and 4 percent iron while the effluent solution has a Y of 0.5 and 4.2 percent iron.

5.2.2.2 Regenerator Section - Pit and Continuous

As the regeneration reaction is conducted in a separate vessel for both the pit and continuous leaching concepts, it is possible to optimize the design for that purpose. This is in contrast to the fine coal process wherein both the leaching and regeneration reactions take place concurrently in the same vessel, necessitating off-optimum conditions for each. As mentioned earlier, the leach solution is actually a 10 percent fine coal slurry therefore both regenerator designs must incorporate sufficient mechanical agitation to maintain the slurry and minimize settling tendencies.

The pit reactor, being a batch-mode operation, will deplete the leach solution to different degrees throughout the period of the leach reaction. This in turn imposes a variable load on the regenerator with the peak load occurring at the start of the leaching reaction. The regenerator has been sized to accommodate the peak, resulting in excess capacity for the major portion of the coal reaction period.

As a result of a trade-off/optimization study, the regenerator for the pit reactor process has been sized at a total capacity of 62,000 cubic feet at a working pressure of 150 psia and a working temperature of 250°F. The vessel is rubber and acid brick-lined and contains three wier-separated stages of equal volume. The vessel accepts the 1620 TPH of leach solution flow rate required by the pit reactor and regenerates it to a minimum Y = 0.95.

The regenerator required by the continuous reactor is designed to accept a constant input Y of 0.5 and to regenerate the leach solution to an output level of Y = 0.95. As was the case with the pit system regenerator, the vessel is rubber and acid brick-lined and is designed for a 150 psia working pressure at 250°F, and contains three equal volume stages. However, the leach solution flow rate is lower (1430 TPH) requiring a vessel of about 55000 cubic feet.

Both regenerators are operated at well over the atmospheric boiling point of the solution and are therefore good sources of low-pressure steam. In addition to process heat, a portion of the low-pressure steam is used to drive an aspirator which pulls a mild vacuum on the two fines filters, as will be discussed in Section 5.2.2.4.

5.2.2.3 Sulfate Removal Section

The reaction with pyrite produces 1.0 mole of iron and 1.2 moles of sulfate from each mole of pyrite reacted. In the fine coal process, Section 5.1.2, the iron and 1.0 mole of the sulfate are removed as $FeSO_4$ while the excess 0.2 mole of sulfate is neutralized with lime to form gypsum. An alternative approach was incorporated in the coarse coal process. This approach involves dissolving scrap-iron into the leach solution by the reaction:

$$0.2\ Fe^{\circ} + 0.4\ Fe^{+3} \rightarrow 0.6\ Fe^{+2} \qquad (22)$$

Then all the reaction products are removed as 1.2 moles of $FesO_4$. This section of the process (see Figure 33) is the same for both the pit and continuous leaching concepts. In processing coarse coal, the best access to the spent leach solution is just downstream of the fines filter (Stream 6, Figure 30) at which time essentially no fines are present. The entire fines-free bleed stream is pumped to a heater conversion tank having a 3-hour residence capacity. This tank is filled with scrap iron. The $Fe^{+3} \rightarrow Fe^{+2}$ conversion is based on an input Y of 0.5 and an effluent Y near zero. The converter effluent stream is pumped to an evaporator/crystallizer

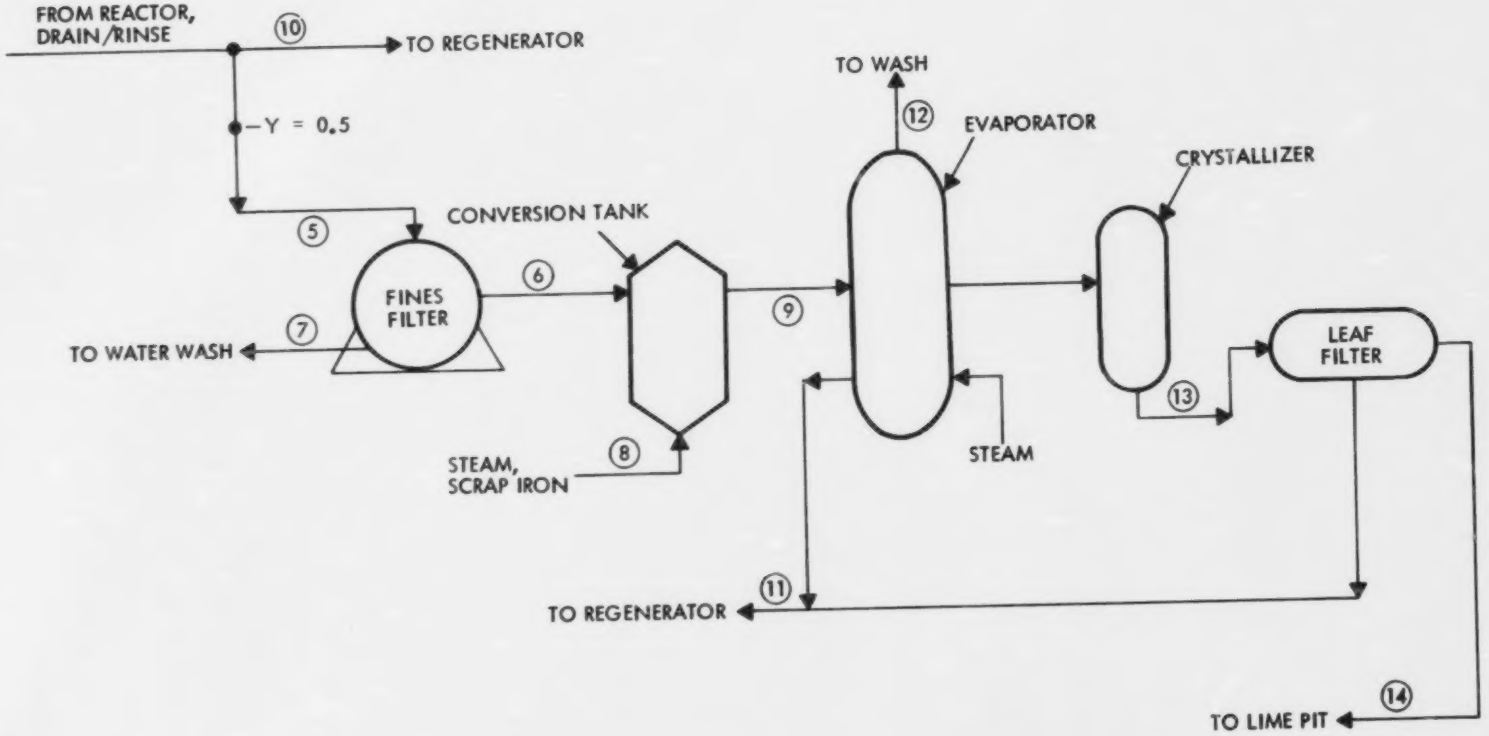

FROM REACTOR, DRAIN/RINSE
⑩
TO REGENERATOR
—Y = 0.5
⑤
CONVERSION TANK
FINES FILTER
⑥
⑦
TO WATER WASH
⑧
STEAM, SCRAP IRON
⑨
TO WASH
⑫
EVAPORATOR
STEAM
CRYSTALLIZER
⑬
LEAF FILTER
⑪
TO REGENERATOR
⑭
TO LIME PIT

Figure 33. Sulfate Removal Section Schematic

train which reduces the water content and increases the iron content to above the saturation level. The overhead water product, Stream 12, is sent to the coal wash line and the salt-laden stream to a leaf filter which separates the Fe^{+2} salt. All residual streams are combined and pumped to the regenerator. The ferrous sulfate salt is sent to disposal.

5.2.2.4 Coal Washing and Filtration Sections

In both the pit and continuous reactor systems, similar schemes for the separation of coal fines and for the washing of the raw leached coal product are envisioned. Fine coal must be separated at two points in each of the conceptual designs (see Figure 30). The first provides a means of controlling the fines content of the leach solution at a maximum of 10 percent; this involves filtration of the spent leach solution bleed stream, using a drum-type vacuum filter. The wet fines cake is conveyed to the water wash line and the filtrate is transferred to the excess salt removal section.

The second fines recovery operation, again employing a rotary drum vacuum filter, operates on the wash water circuit (Stream 19, Figure 30). This filter separates a water-wet fines cake which is transported to the dryer. The filtrate is recycled for use as coal rinse.

Analyses of typical 1/4" x 0 coals have indicated that the fines content can be as high as 30 percent of the bulk mass although 15 to 25 percent is typical. The filters were sized in order to accommodate the extreme, but with the understanding that this represents an overcapacity in terms of most applications. It should be noted that considerable in-process separation of fines is to be expected in the reaction, washing, rinsing and centrifugation steps. The degree of fine particle entrapment to be expected is not known at this time. In some instances the fines (in the continuous reactor) may separate upon feeding from the distribution plate, thereby immediately loading the leach circuit return line, in other cases the fines may be carried through to the rinse/wash line and separated at that point. It therefore follows that a degree of overcapacity is warranted throughout the fines removal and transportation operations in order to allow for normal feed coal variations.

5.2.2.5 Sulfur Removal Section

Both the residual water and free sulfur are removed from the coal in a two-stage inert atmosphere dryer system. In the first stage, water amounting to a nominal 16.5 TPH is quantitatively removed as the feed is heated to 480°F. In the second stage the coal mass is held at 480°F for 1 hour to permit distillation of the elemental sulfur. The clean water is recovered, cooled and pumped to the wash train water feed; sulfur is recovered from the inert gas atmosphere and cast into blocks for sale or disposal. The product coal is cooled and transported to a temporary storage area to await on-site use or shipment.

5.2.2.6 Energy Balance

An energy balance around the process indicates it is possible to eliminate all battery limit heat supply requirements with the exception of the dryer. The reactor (either pit or continuous) temperature is maintained by conserving the heat of reaction and by the sensible heat supplied by the freshly regenerated leach solution. The evaporator, conversion tank and crystallizer heat requirements are supplied by the heat captured from the leach solution flash and blowdown vessel. The regeneration reaction is quite exothermic and by operating the regenerator at 150 psi and 250°F, well above the solution boiling point, the subsequent pressure let down to ambient pressure results in the generation of large quantities of low-pressure steam. The quantity of steam is sufficient to operate an ejector which pulls a mild vacuum on the evaporator and the two fine-coal filters and also to fulfill the latent and sensible heat requirements of the hardware items mentioned earlier. The dryer heat requirements, expressed in terms of the quantity of product coal required, were found to be 9.5 TPH coal.

5.2.3 Process Cost Estimate

Processing costs, including both estimates of capital requirements and annualized costs, have been calculated for both the pit and continuous process concepts. The basis for calculation was June 1975 in both instances

For purposes of comparison to process costs for fine coal processing (as presented earlier in Section 5.1.2.2), the plant capital requirement was assumed to be that for a "battery limits" facility. That is, the economics to be presented here do not account for plant off-sites and do not represent a "grass roots" operation. The logic behind this economic treatment, the information sources, and the method of treatment are the same as presented in the fine coal section.

Coarse Coal Capital Cost Estimate

Process cost estimates are presented for the four process schemes employing the two reactor system concepts described earlier. The four approaches, pit, continuous, pit/float-sink combination, and continuous/float-sink combination were evaluated on the basis of a Meyers Process feed rate of 100 TPH coal containing 3.2 percent pyritic sulfur.

The objective of front-end physical separation equipment in the float sink combination options is to isolate a low pyrite segment of the total feed which does not require further treatment and to concentrate the pyrite in a "sink" fraction which can be fed to the coarse coal Meyers Process. Float-sink separation data for approximately 400 Appalachian coals were examined. It was found that on the average each of these coals could be separated into two approximately equal weight portions by float/sink separation in a liquid medium with a specific gravity of 1.3. Further, it was noted that in 227 of the coals the float fraction contained less than 1 percent total sulfur. For these 227 coals the data shows that the 1.3 specific gravity "float" fraction amounts to nearly 55 percent of the 3/8 inch by zero sample with a standard deviation of about 15 percent. The average total sulfur content of this float fraction is 0.8 percent with a standard deviation of 0.1 percent

Float-sink equipment trains are presently in widespread use, but use higher specific gravity media to achieve float fractions in the 90 percent range, thereby minimizing losses and maximizing the saleable product. It is apparent that if a separation were made at low specific gravity as suggested above but without the benefit of a Meyers Process for treating the "sink" fraction, the gross effect would be a virtual doubling of coal prices as well as the generation of about five times as much spoil requiring acceptable disposal.

In combining the float-sink treatment with the Meyers coarse coal process it was assumed that a 50-50 float-sink division of the feed would represent a reasonable design value, based on the analysis described above. Further analysis of these coals indicated that the sink fraction to be used as process feed would contain about 3.8 percent pyritic sulfur. In a commercial application an economic trade-off would be made at this point to establish the most advantageous position in terms of the adviseability of blending the "float" fraction with the process product (thereby reducing the degree of pyrite removal in the process) versus adjustment of the media specific gravity to control the quantity of "sink" fraction fed to the process. In the conceptual designs considered here, no reblending is considered in order to facilitate direct comparison with the fine coal process.

An equipment list detailing installed equipment costs has been prepared for 100 TPH pit and continuous coarse coal battery limits process options and is presented in Table 32. As may be seen, the installed equipment capital required for the pit process option is $4.17 million while that required for the continuous process option is about 50 percent higher. It should be noted that for the pit and continuous battery limits processes, the reactor sections account for approximately $1.54 million and $3.95 million, respectively, or 37 percent and 60 percent of the total capital requirement (compared to 48 percent for the fine coal processing base case). The additional installed capital investment required for the addition of float-sink options is estimated to be $.42 million.

Operating Cost Estimate

The process operating costs have been estimated for the four options and are summarized in Table 33. It may be seen that the operating costs for the coarse coal options range from $2.94 per ton of coal processed to $6.28 per ton. These are comparable to the $8.94 per ton determined for the fine coal processing scheme (Section 5.1.2.2). However, it must be stressed that the operating costs presented in Table 33 are based on process designs with slightly varying bases. These differences are the following:

TABLE 32. COARSE COAL PROCESS EQUIPMENT LISTS

Item	Pit Reactor $1000	Continuous Reactor $1000
Reactor	728	3175
Regenerator and Exchanger	658	625
Compressor	6	6
Wash Vessel	91	91
Centrifuge	79	79
Knock-out Pot	10	10
Regenerator Agitators	106	106
Flash Vessel and Exchanger	21	21
Regenerator Pumps	8	8
Leach Solution Storage	18	24
Leach Surge Tank	8	8
Iron Conversion Tank	24	24
Iron Conversion Tank Exchanger	70	70
Iron Conversion Tank Pump	2	2
Fines Filter (Leach Circuit)	65	65
Salt Filter (Plate)	32	32
Evaporator	556	556
Crystallizer	71	71
Fines Cake Conveyors (2)	11	11
Crystallizer Feed/Exit Pumps	4	4
Evaporator Feed/Exit Pumps	11	11
Evaporator/Filter Ejector	12	12
Evaporator Condensate Vessel	4	4
Coal Rinse Conveyor and Sump	62	62
Wash Water Feed/Exit Pumps	6	6
Wash Rack Pump	1	1
Centrifuge Fines Filter	64	64
Wash Vessel Drain Conveyor	30	30
Centrifuge Liquid Exit Pump	1	1
Sulfur Trap	18	18
Evaporator and Dryer Condensate Hold Tank	12	12
Dryer (2 Units)	1381	1381
Process Equipment TOTALS	4,170	6,590

TABLE 33. ANNUALIZED COSTS FOR BATTERY LIMITS DESULFURIZATION PLANTS

Cost Element - \$1000/Yr	PROCESS OPTION				
	Pit Reactor Process[a]	Continuous Reactor Process[a]	Pit/Float-Sink Combination[b]	Continuous/Float-Sink Combination[b]	Fine Coal Process[a]
Capital Related Costs Depreciation - 10%	417	659	459	701	1,326
Maintenance, Insurance, Taxes	626	989	689	1052	1,989
Labor	900 (6 Positions)	900 (6 Positions)	1,200 (8 Positions)	1,200 (8 Positions)	1,200 (8 Positions)
Utilities					
Electricity (25 Mil/KW-HR)	600 (3,000 KW)	600 (3,000 KW)	700 (3,500 KW)	700 (3,500 KW)	1,500 (7,500 KW)
Heating-Coal Equivalent	(9 TPH) (247 MM Btu/Hr)	(9 TPH) (247 MM Btu/Hr)	(9 TPH) (247 MM But/Hr)	(9 TPH) (247 MM Btu/Hr)	(4 TPH) (97 MM Btu/Hr)
Water-Process and Cooling	458[c]	458[c]	458[c]	458[c]	241[c]
Materials					
Oxygen 99.5% (\$25/Ton)	800	800	800	800	780
Lime (\$28/Ton)	112	112	112	112	112
Scrap Iron (\$50/Ton)	280	280	280	280	-
TOTAL	4,193	4,798	4,698	5,303	7,148
Cost/Ton Feed - \$/Ton	\$5.25/Ton	\$6.01/Ton	\$2.94/Ton	\$3.31/Ton	\$8.94/Ton
% Coal Yield (Weight Basis)[d]	85%	85%	92%	92%	90%
% Coal Yield (Btu Basis)[d]	90%	90%	95%	95%	94%

[a] Requirements for 100 TPH coal feed

[b] Requirements for 200 TPH combined coal feed

[c] Based on evaporation to reject waste heat

[d] Coal yield values reflect the heating requirements of the process

1) The pit reactor, continuous reactor and fine coal processes are 100 TPH processing facilities for 3.2 percent pyritic sulfur coal while the two float-sink options are 200 TPH units using cleaned coal.

2) The pit/float-sink and continuous/float-sink processes assume the feed coal was precleaned to about 2 percent pyritic sulfur prior to gravity separation. The resultant gravity separated fractions are assumed to contain 3.8 percent pyritic sulfur (Meyers Process treated) and less than 0.5 percent pyritic sulfur (by-passed around the Meyers Process).

The coal yield data (weight basis) presented in Table 33 indicates a higher yield for the combined float-sink options (92 percent) than for the pit and continuous reactor processes options (85 percent). This is based on the design criteria that all of the material bypassed around the Meyers Process, 50 percent of the 200 TPH feed, is 100 percent recovered and blended with coarse coal Meyers Process product. The coal yield in terms of energy recovery is also based on the above stated design criteria.

5.3 PROJECTION OF PROCESS ECONOMICS

Several Meyers Process options were evaluated to determine their overall process economics. The processing options evaluated included both fine and coarse coal approaches (Sections 5.1 and 5.2) integrated into grass roots coal desulfurization facilities. This section presents a description of the various integrated process options, a discussion of the economics evaluation approach, and results of the analyses.

5.3.1 Processing Option Description

The integrated desulfurization facilities include all battery limits Meyers Process equipment in either fine or coarse coal treatment configuration, discussed in Sections 5.1 and 5.2 plus the required off-sites. The off-sites include such items as:

- Feed and product coal storage, handling and transport equipment.
- Physical coal cleaning facilities and size separation equipment.
- By-product handling and storage facilities.
- Waste treatment (physical cleaning and process generated) and storage facilities.
- Process water treatment, storage and pumping facilities.
- Cooling water treatment and pumping equipment.
- Power and steam generation facilities.
- Site office buildings and shop structures.
- Other site improvements such as roads, fences, railroad spurs, etc.

It should be noted that the economic evaluations do not include land costs and assume that oxygen is purchased as an over-the-fence utility item (i.e., neither battery limit nor off-site equipment include an oxygen plant).

For purposes of economic evaluation, four differing process configuration cases were developed. The central basis for each case was a 100 ton per hour Meyers Process unit. A brief description of each case is presented below and block diagrams containing simplified mass balances for each case are presented in Figure 34.

Case 1 - Cleaned Fine Coal Case

Run-of-mine (ROM) coal is physically cleaned and then reduced to 14 mesh top size. The unit feed rate is 120 tons per hour of coal containing about 20 percent ash and 3 to 4 percent pyritic sulfur. The cleaning plant refuse (20 tons per hour) is assumed to contain approximately 75 percent ash and 10 to 14 percent pyritic sulfur. The Meyers

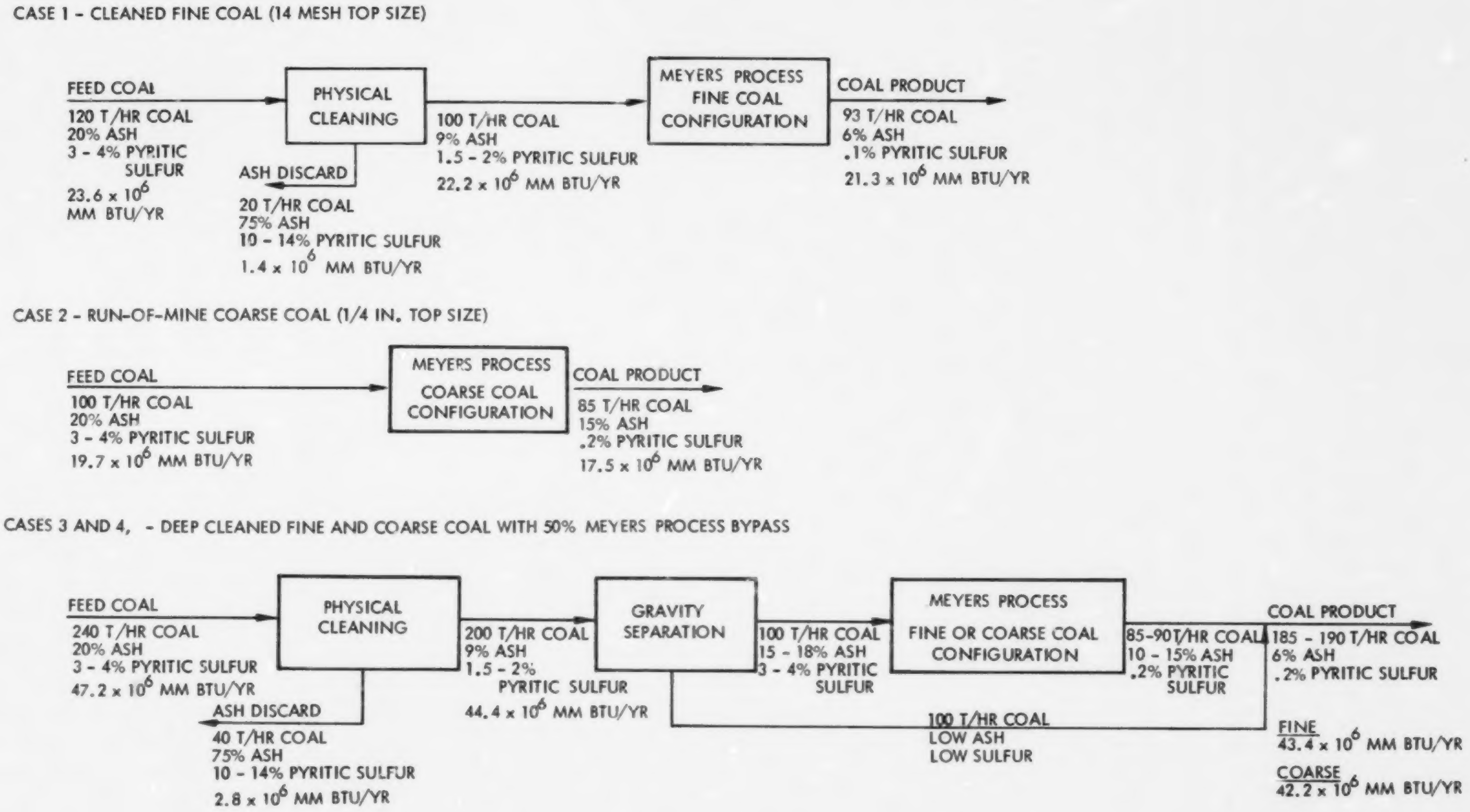

CASE 1 - CLEANED FINE COAL (14 MESH TOP SIZE)
FEED COAL
120 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
23.6 x 10^6 MM BTU/YR
PHYSICAL CLEANING
ASH DISCARD
20 T/HR COAL
75% ASH
10 - 14% PYRITIC SULFUR
1.4 x 10^6 MM BTU/YR
100 T/HR COAL
9% ASH
1.5 - 2% PYRITIC SULFUR
22.2 x 10^6 MM BTU/YR
MEYERS PROCESS FINE COAL CONFIGURATION
COAL PRODUCT
93 T/HR COAL
6% ASH
.1% PYRITIC SULFUR
21.3 x 10^6 MM BTU/YR
CASE 2 - RUN-OF-MINE COARSE COAL (1/4 IN. TOP SIZE)
FEED COAL
100 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
19.7 x 10^6 MM BTU/YR
MEYERS PROCESS COARSE COAL CONFIGURATION
COAL PRODUCT
85 T/HR COAL
15% ASH
.2% PYRITIC SULFUR
17.5 x 10^6 MM BTU/YR
CASES 3 AND 4, - DEEP CLEANED FINE AND COARSE COAL WITH 50% MEYERS PROCESS BYPASS
FEED COAL
240 T/HR COAL
20% ASH
3 - 4% PYRITIC SULFUR
47.2 x 10^6 MM BTU/YR
PHYSICAL CLEANING
ASH DISCARD
40 T/HR COAL
75% ASH
10 - 14% PYRITIC SULFUR
2.8 x 10^6 MM BTU/YR
200 T/HR COAL
9% ASH
1.5 - 2% PYRITIC SULFUR
44.4 x 10^6 MM BTU/YR
GRAVITY SEPARATION
100 T/HR COAL
15 - 18% ASH
3 - 4% PYRITIC SULFUR
MEYERS PROCESS FINE OR COARSE COAL CONFIGURATION
85-90T/HR COAL
10 - 15% ASH
.2% PYRITIC SULFUR
100 T/HR COAL
LOW ASH
LOW SULFUR
COAL PRODUCT
185 - 190 T/HR COAL
6% ASH
.2% PYRITIC SULFUR
FINE
43.4 x 10^6 MM BTU/YR
COARSE
42.2 x 10^6 MM BTU/YR

Figure 34. Process Economics Case Block Diagram

Process feed consists of 100 tons per hour of coal containing approximately 9 percent ash and 1.5 to 2 percent pyritic sulfur. The fine coal Meyers Process configuration utilized in this case is essentially that previously described in Section 5.1.2 with the exception that the reaction and filtra-associated equipment requirements are significantly reduced due to expected reaction rate improvements (2 to 3 times ROM fine coal processing base case described in Section 5.1.1) and lowered ash contents. The processing uses about 100 MM Btu/hr equal to about 4 TPH and the pyrite removed equals 3 TPH. Therefore the product rate is 93 tons per hour of coal containing about 6 percent ash and 0.1 percent pyritic sulfur (93-95 percent removal of pyritic sulfur).

Case 2 - ROM Coarse Coal Case

ROM 1/4 inch top size coal is fed directly to a coarse coal continuous Meyers Process (described in Section 5.2). The coal feed rate is 100 tons per hour and the coal consists of 20 percent ash and 3 to 4 percent pyritic sulfur. Processing removes about 6 TPH of pyrite and requires about 9 TPH of coal to supply the 250 MM Btu/hr required for process heat. The pyritic sulfur is approximately 90-95 percent removed yielding a product rate of 85 tons per hour of coal containing 15 percent ash and about 0.2 percent pyritic sulfur.

Case 3 - Deep Cleaned Fine Coal with 50 Percent Meyers Process Bypass

ROM coarse coal containing 20 percert ash and 3 to 4 percent pyritic sulfur is fed to a physical cleaning plant at a rate of 240 tons per hour. The ash discard (40 tons per hour) contains 75 percent ash and 10 to 14 percent pyritic sulfur. The cleaned coal containing 9 percent ash and 1.5 to 2 percent pyritic sulfur is fed to a gravity separation unit at a rate of 200 tons per hour. The heavy fraction consists of 100 tons per hour of coal containing 15-18 percent ash and 3 to 4 percent pyritic sulfur while the light portion consists of 100 tons per hour of coal with low ash and pyritic sulfur content. The heavy fraction then reduced to 14 mesh top size and fed to a fine coal Meyers Process unit (described in Section 5.1) which produces 90 tons per hour of product coal containing 10-13 percent ash and 0.2 percent pyritic sulfur. The Meyers Process product when blended with the bypassed light coal fraction yields a combined product stream of 190 tons per hour of coal containing about 6 percent ash and 0.2 percent pyritic sulfur (overall 90-95 percent removal of pyritic sulfur from feed coal).

Case 4 - Deep Cleaned Coarse Coal with 50 Percent Process Bypass

Two hundred and forty tons per hour of 1/4 inch top size ROM coal is treated as previously discussed in Case 3. The only difference in the treatment scheme is that a continuous coarse coal Meyers Process configuration (discussed in Section 5.2) is utilized. The coarse coal process requires more coal for internal process heat and therefore yields only 185 TPH of product.

5.3.2 Economics Model Description

The technique used in capitalizing the process options (Cases 1, 2, 3 and 4) is a primary determinant in calculating the unit price of the product. Both utility financing and investor financing methods were considered in determining the price of the product coal.

The method used to determine the product cost for the different financing techniques was based on the technique used by the FPC Synthetic Gas-Coal Task Force in their report on synthetic gas.[11] The applicable equations used in this analysis are summarized below.

The investor capitalization method used in this analysis was the "Discounted Cash Flow" (DCF) financing method with an assumed discounted cash flow rate of return of 20 percent after taxes. In essence, this technique determines the annual revenue during the plant life which will generate a discounted cash flow equal to the total capital invested for the plant. For this analysis, it was assumed that the total capital requirement was used prior to the plant start-up. Other assumptions used in this analysis include the following:

- Plant life was assumed to be 20 years with no cash value at the end of life.

- A straight line method was used to calculate annual depreciation.

- Operating costs and working capital requirements were assumed to be constant during the life of the process.

- Annual revenue and production were assumed to be constant during plant life (i.e., no start-up period).

- The present value of the investment includes the cost of capital during the construction period. The construction period cost of capital, I_C, was approximated by the following expression:

  $$I_C = 1.875\ (0.01r)\ (C-W),$$

  where r is the discounted rate of return (percent), C is the total capital requirement ($MM) and W is the annual working capital ($MM).

- 100 percent equity capital.

Using the above assumptions to modify the basic equations, the required annual revenue requirements for the DCF method can be calculated from the expression given for total capital requirements:

$$C + I_C = \left[(R_I - (N + D)) \left(1 - \frac{T}{100} \right) + D \right] F_{An} + Wf_{pv},$$

where,

C = Total capital requirement, $MM,

R_I = Annual revenue requirement for DCF investor financing, $MM,

D = Annual depreciation, $MM,

F_{An} = Annuity factor for the life of the process at the DCF rate of return,

W = Annual working capital, \$MM,

f_{pv} = Single payment present value factor at the DCF rate of return for a single quantity at the end of the plant life,

N = Net annual operating costs of the plant operation (excluding depreciation), and

T = Annual income tax rate, percent.

As a regulated industry, the utility industry has different capitalization, tax and return-on-investment requirements which differ significantly from a nonregulated industry. The basic equations derived in Appendix I of the referenced document were used along with all of the applicable investor financing assumptions listed above. In addition, the following assumptions were made for the utility financing calculations and were obtained directly from Appendix I of the FPC report:

- The debt/equity ratio was assumed to be 75/25.
- The interest on the debt was assumed to be 9 percent.
- The required return on the equity was assumed to be 15 percent.
- The corresponding return on rate base is 10.5 percent.

Because the rate base for utility financing varies during the life of the plant, this would result in a variable revenue flow (and subsequent coal price) for each year of operation. For this analysis, an average coal price during the plant life was calculated to provide a basis of comparison. Based on this assumption, the average annual revenue requirement could be calculated from the following expression:

$$R_u = N + 0.05\ (C-W) + 0.01 \left[p + \frac{T}{100 - T} (1-d) r_u \right] \left[C - 0.5\ (C-W) \right],$$

where N, C, W and T are the same as for the investor financing, and

R_u = Average annual revenue requirement for utility financing,

p = Return on rate base, percent per year,

d = Debt fraction (0.75), and

r_u = Return on equity, percent per year.

The capitalization requirements were obtained from integrated Meyers Process cost estimates which were based on June 1975 dollars.

All process capital cost data are based on the detailed cost estimates for battery limits Meyers Process units sized for 100 tons per hour of coal feed (presented in Sections 5.1 and 5.2). The battery limits cost for each specific economics case was adjusted to account for the varying coal input compositions and characteristics. For instance, the battery limits fine coal Meyers Process unit cost estimated for Case 1, is significantly less ($5 MM less) than that presented in the base case cost estimate (Section 5.1.2.2). This cost adjustment is warranted due to increased reaction rates (2 to 3 times base case), faster filtration rates observed for cleaned coal and lower circulating gas rates in the sulfur vaporization section. These increased rates lead to less capital investment in reactor, filter and sulfur removal associated operations.

Off-site investment for each of the four cases was estimated as a percentage of the battery limit cost. The basic off-site investment was then adjusted for special characteristics of the case. For fine coal processing, the basic off-site investment was estimated at 50 percent of the battery limits cost given in Table 26 of Section 5.1 or $6.63 million. It was expected that Case 1 would have a reduction in off-site capital relative to the base case resulting from less by-products, waste disposal, power and steam. The reduction was estimated to equal the $0.8-$1.0 million cost for the physical cleaning. Case 2 off-sites were estimated to be 100 percent of the battery limits cost given in Section 5.2 or $4.2 million. Case 3 has a 240 TPH physical cleaning section and a gravity separation section and grinder with a total estimated capital cost of \$2.5 million. This added to the basic process off-site gives a total off-site cost of \$9.13 million. Case 4 has the physical cleaning train and gravity separation without grinding. This gives a total off-site capital estimate of \$6.5 million.

Operating costs were estimated from base case operating costs. Adjustments were made to account for such things as varying oxygen and chemicals (lime and scrap iron) requirements due to varying Meyers Process feed pyritic sulfur contents. The operating labor requirement was adjusted to properly reflect the varying complexities represented by the four cases. Disposal costs were estimated for each case to reflect the differing requirements (primarily due to the use of physical cleaning in some cases and not in others and Meyers Process operation with coals of varying pyritic sulfur content). Disposal costs were estimated to be \$5.90 per ton of refuse.

All other capital related and operating related costs were determined as percentages of estimated battery limit costs, off-site equipment costs, raw materials costs, and labor costs. Table 34 presents a summary of the economic evaluation criteria.

The economic evaluation criteria given in Table 34 and the annualized revenue expressions for investor and utility financed process plants described in this section can be combined to give an expression of the following form:

$$P = (aX + bY + cZ)/d$$

where,

P = is the required sales price for processed coal, \$/MM Btu
X = working capital for raw materials and supplies, \$
Y = sum of the total plant investment and start-up cost, \$
Z = annual total operating cost, \$/year
a, b, c = constants given in Table 35
d = annual energy output, MM Btu/yr

TABLE 34. ECONOMIC EVALUATION CRITERIA

Operating Cost Criteria

Raw material - coal @ $10/ton, $20/ton, $30/ton

Utilities
- Electricity @ 2.5¢/kw-hr
- Oxygen @ $25/ton
- Cooling water @ 5¢/1000 gal.
- Process water @ 25¢/1000 gal.

Chemicals
- Lime @ $28/ton
- Scrap iron @ $50/ton

Disposal @ $5.90/ton of refuse

Labor
- Process operating labor @ positions/shift x 8304 man-hours/yr x $5/man-hour
- Maintenance labor @ 1.5%/yr of total plant investment
- Supervision @ 15% of operating labor and maintenance labor
- General overhead and administration at 60% of labor and supervision

Supplies
- Operating @ 30% of process operating labor
- Maintenance @ 1.5% of total plant investment

Taxes and insurance @ 2.7%/yr of total plant investment

Total operating cost = sum of raw material + utilities + chemicals + disposal + labor + supplies + taxes and insurance

Capital Cost Criteria

Battery limits capital as discussed in text

Off-site capital as discussed in text

Overhead and profit @ 22% of battery limits + off-sites

Engineering and design @ 10% of battery limits + off-sites

Contingency @ 15% of battery limits + off-sites + overhead and profit + engineering and design

Total plant investment = sum of battery limits + off-sites + overhead and profit + engineering and design + contingency

Interest for construction @ 9% of total plant investment x 1.875

Start-up cost @ 20% of total operating costs

Working capital = sum of raw materials inventory of 60 days at full rate + materials and supplies at 0.9% total plant investment + 1/24 annual product revenue

TABLE 35. CONSTANTS FOR USE IN ECONOMICS EVALUATIONS

	Investor Financing	Utility Financing
a	.391	.140
b	.505	.121
c	1.016	1.006

5.3.3 Process Economics Evaluations

The process economics evaluations were carried out as described in the previous section. The results of those evaluations are presented in Tables 36, 37, 38, and 39. Calculations were performed at three assumed ROM coal costs and using both utility and investor financing criteria. Coal costs of $10 per ton, $20 per ton and $30 per ton were selected since they represent the broad range of currently reported ROM coal costs ($10 per ton at mine mouth to $25 per ton reported delivered price at some plant sites). As may be determined from the data, the required market value of the treated coal ranges from a low of 66¢/MM Btu for Case 4 (assuming $10/ton ROM coal cost and utility financing) to a high of $2.39/MM Btu for Case 1 (assuming $30/ton ROM coal cost and investor financing). In all cases, utility financing yielded market costs on the order of 60 percent to 80 percent of market costs required when utilizing investor financing.

An equivalent upgrading cost has also been determined. The upgrading cost is found by deducting the cost of the dirty energy ($.41/MM Btu for 20% ash, 3-4 percent sulfur coal at $10/ton; $.81 at $20/ton and $1.22 at $30/ton) from the cost shown in Tables 36 through 39 for the clean energy ($.66 to $2.39/MM Btu). These upgrading or processing costs, which range from $.25/MM Btu to $1.17/MM Btu, are presented in Table 40. For all cases the processing cost includes ash reduction as well as sulfur reduction. Except for Case 2, physical cleaning was assumed to be coupled with pyrite removal which results in a major reduction in ash from about 20 percent to about 6 percent.

TABLE 36. CASE 1, CLEANED FINE COAL

Product Annual
Energy Value, 21.3 x 10^6 MM Btu/yr

	ROM Coal Cost		
Capital Related Requirements, $MM	$10/Ton	$20/Ton	$30/Ton
Battery Limit Capital	8.26	8.26	8.26
Off-site Capital	6.63	6.63	6.63
Overhead and Profit	3.28	3.28	3.28
Engineering and Design	1.49	1.49	1.49
Contingency	2.95	2.95	2.95
Total Plant Investment(1)	22.61	22.61	22.61
Interest for Construction	3.82	3.82	3.82
Start-up Costs	2.89	4.81	6.73
Working Capital (Utility Financing)	2.54	4.57	6.59
Working Capital (Investor Financing)	2.98	5.05	7.12
Total Capital Related Costs (Utility)	31.86	35.81	39.75
Total Capital Related Costs (Investor)	32.30	36.29	40.28
Operating Costs, $MM/Yr			
Raw Material (Coal)	9.60	19.20	28.80
Chemicals (Lime, Scrap)	.06	.06	.06
Supplies	.50	.50	.50
Disposal	.42	.42	.42
Utilities	1.63	1.63	1.63
Labor (13 Positions)	1.62	1.62	1.62
Taxes and Insurance	.61	.61	.61
Total Operating Costs	14.44	24.04	33.64
Required Coal Market Price, $/MM Btu			
Utility Financing	.84	1.31	1.79
Investor Financing	1.33	1.86	2.39

---

(1) Equivalent to a plant capital investment of $79.60/kw.

TABLE 37. CASE 2, ROM COARSE COAL

Product Annual
Energy Value, 17.5 x 10^6 MM Btu/yr

	ROM Coal Cost		
Capital Related Requirements, $MM	$10/Ton	$20/Ton	$30/Ton
Battery Limit Capital	4.20	4.20	4.20
Off-site Capital	4.20	4.20	4.20
Overhead and Profit	1.85	1.85	1.85
Engineering and Design	.84	.84	.84
Contingency	1.66	1.66	1.66
Total Plant Investment(1)	12.75	12.75	12.75
Interest for Construction	2.15	2.15	2.15
Start-up Costs	2.51	4.11	5.71
Working Capital (Utility Financing)	2.06	3.74	5.42
Working Capital (Investor Financing)	2.33	4.05	5.77
Total Capital Related Costs (Utility)	19.47	22.75	26.03
Total Capital Related Costs (Investor)	19.74	23.06	26.38
Operating Costs, $MM/Yr			
Raw Material (Coal)	8.00	16.00	24.00
Chemicals (Lime, Scrap)	.39	.39	.39
Supplies	.30	.30	.30
Disposal	.64	.64	.64
Utilities	1.86	1.86	1.86
Labor (9 Positions)	1.02	1.02	1.02
Taxes and Insurance	.34	.34	.34
Total Operating Costs	12.55	20.55	28.55
Required Coal Market Price, $/MM Btu			
Utility Financing	.84	1.32	1.80
Investor Financing	1.20	1.74	2.28

---

(1) Equivalent to a plant capital investment of $54.60/kw.

TABLE 38. CASE 3, DEEP CLEANED FINE COAL WITH 50% MEYERS PROCESS BYPASS

Product Annual Energy Value, 43.4 x 10^6 MM Btu/yr		ROM Coal Cost	
Capital Related Requirements, $MM	$10/Ton	$20/Ton	$30/Ton
Battery Limit Capital	13.26	13.26	13.26
Off-site Capital	9.13	9.13	9.13
Overhead and Profit	4.93	4.93	4.93
Engineering and Design	2.24	2.24	2.24
Contingency	4.43	4.43	4.43
Total Plant Investment(1)	33.99	33.99	33.99
Interest for Construction	5.74	5.74	5.74
Start-up Costs	5.28	9.12	12.96
Working Capital (Utility Financing)	4.83	8.88	12.92
Working Capital (Investor Financing)	5.51	9.66	13.80
Total Capital Related Costs (Utility)	49.84	57.73	65.61
Total Capital Related Costs (Investor)	50.52	58.51	66.49
Operating Costs, $MM/Yr			
Raw Material (Coal)	19.20	38.40	57.60
Chemicals (Lime, Scrap)	.11	.11	.11
Supplies	.69	.69	.69
Disposal	.84	.84	.84
Utilities	2.62	2.62	2.62
Labor (14 Positions)	2.01	2.01	2.01
Taxes and Insurance	.92	.92	.92
Total Operating Costs	26.39	45.59	64.79
Required Coal Market Price, $/MM Btu			
Utility Financing	.73	1.20	1.66
Investor Financing	1.11	1.63	2.15

---

(1) Equivalent to a plant capital investment of $58.70/kw.

TABLE 39. CASE 4, DEEP CLEANED COARSE COAL WITH 50% MEYERS PROCESS BYPASS

Product Annual
Energy Value, 42.2 x 10^6 MM Btu/yr

	ROM Coal Cost		
Capital Related Requirements, $MM	$10/Ton	$20/Ton	$30/Ton
Battery Limit Capital	4.20	4.20	4.20
Off-site Capital	6.50	6.50	6.50
Overhead and Profit	2.35	2.35	2.35
Engineering and Design	1.07	1.07	1.07
Contingency	2.11	2.11	2.11
Total Plant Investment(1)	16.23	16.23	16.23
Interest for Construction	2.74	2.74	2.74
Start-up Costs	4.92	8.76	12.60
Working Capital (Utility Financing)	4.51	8.55	12.59
Working Capital (Investor Financing)	4.89	9.04	13.18
Total Capital Related Costs (Utility)	28.40	36.28	44.16
Total Capital Related Costs (Investor)	28.78	36.77	44.75
Operating Costs, $MM/Yr			
Raw Material (Coal)	19.20	38.40	57.60
Chemicals (Lime, Scrap)	.39	.39	.39
Supplies	.38	.38	.38
Disposal	.96	.96	.96
Utilities	1.96	1.96	1.96
Labor (11 Positions)	1.29	1.29	1.29
Taxes and Insurance	.44	.44	.44
Total Operating Costs	24.62	43.82	63.02
Required Coal Market Price, $/MM Btu			
Utility Financing	.66	1.14	1.62
Investor Financing	.88	1.41	1.95

---

(1) Equivalent to a plant capital investment of $28.80/kw.

TABLE 40. UPGRADING (PROCESSING) COSTS

	ROM Coal Cost $10/Ton	 $20/Ton	 $30/Ton
Case 1			
Utility Financed	$.43/MM Btu	$.50/MM Btu	$.57/MM Btu
Investor Financed	$.92/MM Btu	$1.05/MM Btu	$1.17/MM Btu
Case 2			
Utility Financed	$.43/MM Btu	$.51/MM Btu	$.58/MM Btu
Investor Financed	$.79/MM Btu	$.93/MM Btu	$1.06/MM Btu
Case 3			
Utility Financed	$.32/MM Btu	$.39/MM Btu	$.44/MM Btu
Investor Financed	$.70/MM Btu	$.82/MM Btu	$.93/MM Btu
Case 4			
Utility Financed	$.25/MM Btu	$.33/MM Btu	$.40/MM Btu
Investor Financed	$.47/MM Btu	$.60/MM Btu	$.73/MM Btu

6. CHEMICAL ANALYSIS STUDIES

The chemical analysis studies had two objectives: (1) to experimentally investigate the adequacy of established coal sulfur analysis techniques for the accurate determination of Meyers Process performance and (2) to identify and screen potential Meyers Process efficiency monitoring techniques for use in full-scale operations. The need for these studies was dictated by frequent inconsistencies in sulfur analysis data derived from processed coal and by the desirability to identify process monitoring techniques which are simpler and faster than the standard ASTM coal sulfur analysis methods.

In the Meyers Process the pyritic sulfur in coal is oxidized to elemental sulfur and sulfate by the reduction of ferric ions to the ferrous state; the latter are regenerated to the ferric ~~state by oxygen~~. The sulfate sulfur product dissolves in the reagent solution. The elemental sulfur can be recovered by extraction with hydrocarbon solvents (e.g., toluene or naphtha) or by vaporization; in bench-scale experimentation hydrocarbon leaching was used almost exclusively. Thus, Meyers Process chemistry permits, in principle, the use of three independent approaches for the estimation of process performance all of which involve standardized chemical analysis techniques. The most direct approach is the determination of pyrite in coal before and after processing. The second approach involves the determination of total sulfur in coal before and after processing. The third approach is based on the estimation of ferrous ion production during leaching. Since 10.2 moles of ferrous ion are produced per mole of pyrite leached, this approach of measuring the performance of the process is very accurate provided the leaching reaction is totally selective, as it is with most coals, or ferrous ion production from side reactions can be independently estimated. This approach is also an excellent means of monitoring process performance during processing because it is simple and quick. Unfortunately, it is only useful when the leaching and regenerations operations are performed separately whereas simultaneous leaching-regeneration is contemplated for most coals.

In principle, the first two approaches are equivalent since the Meyers Process should not affect the organic sulfur in coal and it should have insignificant effect on the sulfate sulfur concentration of unweathered coal which normally is 0.1 wt. percent or less. In practice, direct equivalency of these two approaches has been very inconsistent and infrequent. Probable causes for the observed inconsistencies may be grouped into three categories: (1) performer inconsistencies in the analyses of coal, a very real possibility with processed coal, the sulfur content of which is low, (2) incomplete recovery of process sulfur products or high sulfate starting coal (weathered coal), and (3) inadequacy of standard coal sulfur analyses techniques to accurately determine the sulfur and sulfur forms content of processed coal (Meyers Process effects on sulfur analysis techniques). Though much of the evidence from hundreds of coal analyses pointed to performer inconsistency as the most probable cause for inconsistencies in analysis data, there was sufficient uncertainty in such conclusion to warrant investigation of probable Meyers Process effects on standard sulfur analysis techniques.

The investigation of the coal sulfur analysis problems was combined with the effort to identify efficient process monitoring techniques for use in full scale Meyers Process plants. The results and conclusions are presented in separate sections below.

6.1 ADEQUACY OF STANDARD SULFUR ANALYSIS TECHNIQUES FOR DETERMINING MEYERS PROCESS PERFORMANCE

The total sulfur in ROM, run-of-the-mine, coal is comprised of three sulfur forms: pyritic, sulfate, and organic sulfur. Product coal from the Meyers Process may contain only one or as many as four sulfur forms. Complete leaching of pyrite, complete recovery of process sulfur products (elemental sulfur and sulfate), and dissolution of the sulfate in the ROM would result in processed coal the total sulfur of which is equal to the organic sulfur present in the starting coal. Less than 100 percent leaching of pyrite and sulfate and incomplete recovery of the elemental sulfur product would result in processed coal with four sulfur forms. Pyritic sulfur and sulfate sulfur can be determined directly by standard ASTM techniques. Organic sulfur and unrecovered elemental sulfur are computed as a single value from the difference between the total sulfur content of the coal, determined by Eschka analysis, and the sum of the pyritic and sulfate sulfur values.

The Meyers Process affects only the pyritic sulfur in coal directly unless the coal is severely weathered in which case sulfate removal also occurs during processing. Indirectly, however, the Meyers Process may affect all three sulfur forms in coal because of incomplete sulfur product recovery and because elemental sulfur is computed as organic sulfur. Pyritic sulfur is always reduced; sulfate sulfur remains unchanged or increases slightly during processing, depending on processing conditions, when low sulfate ROM coal is used; organic sulfur remains unchanged unless elemental sulfur recovery is incomplete in which case the "organic" sulfur content of the processed coal should always be higher with the increase being equal to unrecovered elemental sulfur. Thus, in the cases where sulfur removals computed from total sulfur and pyritic sulfur analyses do not agree, the delta in the two sulfur removal values should equal the quantity of unrecovered sulfur product. Complementing the total and pyritic sulfur analyses by the determination of the sulfate sulfur in the sample should lead to the quantitative identification of each of the sulfur forms left on the coal.

The data in Appendices A and B, Volume 2 show that the coal sulfur analyses were infrequently consistent with the above expectations. The discrepancies are manifested in the value of organic sulfur, and they were obviously caused by inaccuracies in analyses either of total sulfur or of one or both of the sulfur forms (pyrite and sulfate). As indicated earlier, the extensive experimentation on the Meyers Process with Lower Kittanning coals has not shown any evidence that the process affects the organic sulfur content of the coal. Thus, indicated reductions in the organic sulfur of coals during processing must be due to errors in analyses. The same conclusion is drawn from coal samples exhibiting relatively large increases in organic sulfur which could not be justified in terms of unrecovered elemental sulfur.

The discrepancies are in the 0.1 to 0.5 wt. percent sulfur range and therefore, of relatively minor importance to the measurement of Meyers Process efficiency when applied to high sulfur, high pyrite coals as the one used in this program (though they are very important in determining whether the processed coal met a specific sulfur standard or not). These discrepancies become very important in the determination of Meyers Process efficiency and rates as the pyrite content of the feed coal to the process decreases (e.g., pyritic sulfur in the 1 to 2 wt. percent range).

Problems with coal sampling and analysis have been encountered by virtually everyone requiring accurate coal composition data on a regular basis. The consensus of opinion (from mine quality control personnel to Bureau of Mines chemists) appears to be that the standard ASTM procedures for coal analysis are adequate when properly utilized, but that the consistency of accurate data suffers when these techniques are applied routinely in an assembly line operation (necessary for holding analysis costs to reasonable levels). The purpose of this task was to investigate whether or not the Meyers Process aggravated these problems by direct effects on the accuracy of standard sulfur analysis procedures. In the case of total sulfur analyses the concern centered on potential effects from organic solvents used to recover elemental sulfur and from unrecovered elemental sulfur itself. In the case of sulfur forms the concern was whether the reflux times specified by the ASTM procedures for sulfate and pyrite recovery were adequate for use on chemically leached coal whose sulfate and pyritic sulfur values are approximately equal and very low.

Three different techniques were used in the total sulfur coal analysis investigations: Eschka, Bomb Wash, and Leco (Eschka being the standard ASTM technique). The rationale was that since these three sulfur analysis techniques differ substantially in procedure it would be very unlikely that the Meyers Process could have the same effect on the accuracy of each of them, if indeed processed coal by the Meyers Process affected established sulfur analysis techniques. Eschka and Bomb Wash are commonly used sulfur analysis techniques for coal; Leco was selected as the third method because it is an adequately developed sulfur analysis technqiue and because it offers the potential for use as a Meyers Process monitoring technique.

The matrix of experiments began with comparison of the three total sulfur analysis methods on NBS certified coal samples ranging in sulfur values from 0.546 to 3.020 wt. percent. The three analyses methods were then used on:

- Run-of-the-mine, ROM, Lower Kittanning coal samples from the coal utilized in this program.
- L-R processed coals at two different reaction times.
- Organic solvent treated L.K. coals (the coal was refluxed for one hour in either hexane, or heptane, or toluene without prior leaching with ferric sulfate).
- ROM and organic solvent treated coals doped with 2 to 3 wt. percent elemental sulfur.

The data generated from these experiments are summarized in Table 41.

The first group of data in Table 41 compares NBS certified total sulfur values to total sulfur analyses performed on the same coal using Eschka, Bomb Wash, and Leco techniques. The ASTM acceptable reproducibility spreads for total sulfur analyses performed on the same coal at two different laboratories are 0.1 wt. percent sulfur for coal containing 2 wt. percent sulfur or less and 0.2 wt. percent sulfur for coal with higher than two percent sulfur content. All three techniques yielded values within the ASTM allowable spreads. Thus, any one of these techniques may be utilized for the determination of sulfur concentration in ROM coals up to at least 3 wt. percent. It should be noted, however, that the Eschka technique yielded values consistently closer to the certified sulfur values. At coal sulfur concentrations in the 2 to 3 wt. percent range the Bomb Wash and Leco technique values indicate a low bias with Leco furnishing the lowest sulfur concentrations. On the basis of these observations, the Eschka technique must be assumed to be the most accurate of the three for analyzing high sulfur coal. However, if the NBS samples were certified by the Eschka technique the above conclusion may be unwarranted.

TABLE 41. COMPARISON OF TOTAL SULFUR ANALYSIS TECHNIQUES (WEIGHT PERCENT SULFUR IN COAL)

I. NBS CERTIFIED COALS:

Certified Values	Eschka	Bomb Wash	Leco
0.546 ± 0.003	0.54 ± 0.02	0.55 ± 0.00	0.59 ± 0.04
2.016 ± 0.014	2.03 ± 0.04	1.92 ± 0.01	1.90 ± 0.03
3.020 ± 0.008	2.94 ± 0.03	2.93 ± 0.03	2.86 ± 0.01

II. ROM (RUN-OF-MINE) LOWER KITTANNING COAL:

	Eschka	Bomb Wash	Leco
	4.43 ± .06	4.24	4.08 ± 0.06

III. L-R PROCESSED LOWER KITTANNING COALS:

Experiment No.	Eschka	Bomb Wash	Leco
S2 (Toluene*)	1.44 ± 0.005	1.52 ± 0.05	1.54 ± 0.02
S3 (Toluene*)	1.49	1.53 ± 0.01	1.54 ± 0.01
S4 (Toluene*)	2.37 ± 0.01	2.39 ± 0.03	2.36 ± 0.005
S5 (Hexane-Toluene**)	2.22 ± 0.04	2.34 ± 0.07	2.33 ± 0.06

IV. ORGANIC SOLVENT TREATED ROM LOWER KITTANNING COAL:

Solvent Used	Eschka	Bomb Wash	Leco
Hexane	4.37	4.28	3.84 ± 0.11
Heptane	4.48 ± 0.05	4.30	4.19 ± 0.08
Toluene	4.32 ± 0.01	4.23	3.95 ± 0.03

V. ROM LOWER KITTANNING COAL DOPED WITH ELEMENTAL SULFUR:

Sample Doped With Elemental Sulfur	Bomb Wash		Leco		Eschka		% Recovery		
	Calculated Sulfur	Analyzed Sulfur	Calculated Sulfur	Analyzed Sulfur	Calculated Sulfur	Analyzed Sulfur	Bomb Wash	Leco	Eschka
ROM Coal	6.96	6.83	6.80	6.53±0.10	7.15	6.96±0.03	98	96	97
Hexane Refluxed	6.97	6.82	6.73	6.44±0.001	7.16	6.77	98	96	95
Heptane Refluxed	7.20	7.20	7.09	6.70±0.01	7.39	7.10±0.06	100	94	96
Toluene Refluxed	7.16	7.11	6.83	6.74±0.00	7.35	7.00	99	99	95

---

* Elemental sulfur on processed coal was extracted by toluene.

** Elemental sulfur on processed coal was extracted first by hexane and then by toluene.

The discrepancy among sulfur values generated by the three techniques investigated in this program becomes meaningful when the total sulfur concentration in the coal exceeds 4 wt. percent, as demonstrated by the second group of data in Table 41. These data were generated on identical samples of ROM Lower Kittanning coal. The spread between Eschka and Leco generated sulfur values is unacceptable (too large to be considered a normal deviation between values of valid sulfur analysis techniques). A careful examination of the procedures prescribed for the Bomb Wash and Leco techniques did not result in the identification of inherent technique shortcomings which could predict the apparent bias toward lower sulfur values. However, small systematic errors in the application of these procedures and defective equipment or operator biases could not be completely discounted as probable causes for the observed low sulfur value bias. On the basis of the available data it must be concluded that the Leco technique can not be used with confidence to determine the sulfur content of coals when it exceeds 3 wt. percent. At lower coal sulfur concentrations the Leco technique exhibited adequate accuracy and excellent reproducibility to render it useful in monitoring the efficiency of the Meyers Process.

The data in Sections III through V in Table 41 represent the results of studies performed to determine if the Meyers Process affects the accuracy of total sulfur determinations on coal. Several samples of L-R processed Lower Kittanning coal from four experiments were analyzed for total sulfur content by each of the three sulfur analysis techniques. The data are summarized in Section III of Table 41. The data show that if the Meyers Process affects the accuracy of total sulfur determinations, its effect is virtually identical on all three techniques. This was considered unlikely and it was, therefore, concluded that the sulfur content of processed coal can be accurately determined by any of the three techniques, if properly used. The validity of this conclusion was verified further by the data in Sections IV and V.

Organic solvents and elemental sulfur are the only substances potentially present in coal subjected to the Meyers Process and not present in the raw coal (the former would be present only if the product elemental sulfur is recovered through organic solvent leaching of the processed coal).

Thus, it was decided to investigate whether organic solvents of potential use to the Meyers Process and whether elemental sulfur not completely recovered from processed coal could measurably affect the accuracy of coal sulfur analysis techniques. Samples of ROM Lower Kittanning coal (Section II, Table 41) with known sulfur content were refluxed for one hour in each of the three organic solvents listed in Table 41 and subsequently analyzed by each of the three total sulfur analysis techniques. Comparison of the data in Sections II and IV reveals that these solvents did not affect the accuracy of sulfur analyses. In separate experiments, ROM coal samples and organic solvent refluxed samples were doped with known quantities of elemental sulfur and then reanalyzed. The data in Section V demonstrate that the elemental sulfur added to the coal was accurately reflected by the total sulfur analyses performed on the coal samples regardless of the analysis technique used.

In summary, the total sulfur analysis investigations revealed that the Meyers Process does not affect the accuracy of coal total sulfur determinations by Eschka, Bomb Wash, or Leco techniques. Within acceptable deviations, these three analysis techniques proved equally accurate in the determination of coal sulfur concentrations up to approximately 3 wt. percent. At higher coal sulfur concentrations the Leco technique demonstrated an unacceptable low bias, yielding sulfur values which were lower by as much as 10 percent than those obtained by Eschka; however, it was not established conclusively whether the low values were inherent to the technique or due to systematic errors in its utilization.

The sulfur forms investigations led also to the conclusion that the Meyers Process does not affect the accuracy of standard coal analysis techniques. In these investigations potential interferences of elemental sulfur on sulfate analyses and sulfate on pyrite analyses were examined.

In the case of elemental sulfur the concern was that, if incompletely recovered, it could be physically leached during the hydrochloric acid extraction and subsequently be oxidized to sulfate in the process of sulfate analysis. Experiments performed on elemental sulfur derived from the

Meyers Process as well as on coal doped with elemental sulfur showed no evidence that this sulfur form oxidizes to sulfate during the standard ASTM procedure for coal sulfate analysis. In addition, sulfur balance data derived from bench-scale experimentation on the Meyers Process indicated that elemental sulfur recovery was virtually complete in the majority of experiments and, therefore, could not account for the apparent inconsistencies in sulfur forms analyses (Section 2, Volume 1 and Appendices A, B, and C, Volume 2 of this report).

A more serious concern was that associated with potential Meyers Process effects on pyrite analysis data, either because of sulfate interference or due to incomplete leaching of pyrite. According to ASTM procedure, pyrite in coal is determined from the difference in the iron content of the nitric acid and hydrochloric acid solutions derived by refluxing for 30 minutes identical coal samples, except for size, in the respective acids. The acid soluble iron compounds of coal, principally iron sulfates and oxides, are leached by the hydrochloric acid; the nitric acid being an oxidizing agent leaches all of the iron in coal which includes the pyritic iron. Normally, the soluble iron in ROM coals represents a small percentage of the pyritic iron; thus, incomplete leaching of the sulfate by hydrochloric acid introduces an insignificant error to the determination of the pyrite content of coal. In processed coal the pyrite content is low and substantial errors in its determination could result from improper leaching of the iron forms in coal, especially in cases where sulfate recovery is incomplete as it was the case in a number of experiments performed during this program (Appendices A and B, Volume 2). The concern was whether the acid reflux times prescribed by ASTM procedures were adequate to remove the iron from coal to the intended extent. The principal question was whether 30 minutes reflux time in hydrochloric acid was sufficient for the leaching of process derived sulfate product (higher concentration and conceivably different form of iron sulfate than typically found in ROM coals).

A summary of the data generated on the effect of acid digestion time on pyritic and sulfate sulfur analyses is presented in Table 42. ASTM and modified ASTM analysis procedures were used in these investigations. The

TABLE 42. COAL SULFUR FORMS ANALYSIS INVESTIGATIONS - COMPARISON OF TECHNIQUES AND EFFECT OF COAL DIGESTION TIME[(a)]

Sample	Digestion (Reflux) Time	Pyritic Sulfur, Wt. %		Sulfate Sulfur, Wt. %		
					Turbidimetric	
		ASTM	AA	ASTM	Peroxide	Bromine
ROM (Weathered)	0.5 Hours	2.66 ± .12	2.76 ± .13	0.61 ± .03		
L. K. Coal	1 Hour	2.66 ± .04	-	0.62 ± .01	0.14 ± .03	0.15 ± .02
	2 Hours	2.63 ± .07	-	0.64 ± .01	0.18 ± .05	0.14 ± .05
	3 Hours	2.56 ± .04	2.61 ± .02	0.67 ± .01	0.24 ± .08	0.24 ± .01
Processed Coal	0.5 Hours	0.39 ± .02	0.38 ± .01	0.29 ± .02	0.16 ± .01	
(Exp. S2)	1 Hour	0.44 ± .01	0.40 ± .04	0.31 ± .01	<0.01	<0.01
	2 Hours	0.41 ± .02	0.39 ± .06	0.35 ± .01	0.16 ± .01	0.19 ± .02
	3 Hours	0.44 ± .02	0.34 ± .05	0.39 ± .02	0.04 ± .01	0.04
Processed Coal	0.5 Hours	1.00 ± .06	1.00 ± .00	0.60	0.27 ± .00	
(Exp. S4)	1 Hour	0.94 ± .04	0.91 ± .04	0.63 ± .01	0.24 ± .02	0.27 ± .04
	2 Hours	1.01 ± .02	0.91 ± .04	0.64 ± .00	0.30 ± .03	0.28 ± .01
	3 Hours	1.07 ± .02	1.07 ± .02	0.65 ± .01	0.19 ± .02	0.31 ± .04
Processed Coal	1 Hour	(0.67),[b] 0.59	(0.64),[b] 0.63	(0.60),[c] 0.61	0.41, 0.61[d]	-
(Exp. S2)	2 Hours	(0.66), 0.57	(0.63), 0.50	(0.60), 0.62	0.33, 0.67[d]	-
Doped with Pyrite	3 Hours	(0.66), 0.57	(0.64), 0.59	(0.60), 0.62	0.37, 0.61[d]	-

NOTES:

(a) All analyses were performed in triplicate; ASTM analyses were performed on 1 gram samples, the AA and turbidimetric on 5 gram samples.

(b) The values in parentheses represent the calculated pyritic sulfur content of the sample (the previously determined pyritic sulfur of the coal by the ASTM and AA techniques, respectively, plus the pyrite added to it).

(c) Calculated sulfate value of sample (ASTM determined sulfate sulfur value of coal + added ferric sulfate).

(d) Cation-exchanged turbidimetric analysis values.

modified techniques are simpler than the corresponding ASTM techniques and in principle more accurate since they eliminate the subjectivity inherent in the determination of titration end points. However, the data in Table 42 do not appear to justify the latter expectation. Both the ASTM and the modified techniques require the acid digestion step. The modified techniques used atomic absorption, AA instead of iron titration in pyrite analyses and turbidimetric instead of gravimetric analyses in sulfate determinations; two different oxidants were used in the turbidimetric sulfate analyses. Comparison of ASTM and AA pyritic sulfur data reveals that the two techniques yielded equivalent values with slightly better reproducibility evident in data generated by the ASTM technique. In multiple sample analyses, the AA technique may merit consideration. The turbidimetric technique yielded consistently low values until a cation exchange column was used to remove interferences (last column of last three rows of data in Table 42). The turbidimetric technique merits serious consideration since it simplifies appreciably the determination of sulfate; however, cation interferences must be eliminated which implies that the technique may require frequent calibrations against gravimetrically derived data.

The first group of data in Table 42 were obtained from analyses performed in triplicate on weathered ROM Lower Kittanning coal. Substantially weathered coal was selected in order that its sulfate content be sufficiently high to detect changes in its determination as a function of digestion time. The data indicate a trent toward lower pyritic sulfur values and correspondingly higher sulfate values with increasing digestion times. The trend appears to be real, but the difference in the determined sulfur form values in coal samples digested for 0.5 and 3 hours, respectively, is within expected analysis reproducibility limits.

The second and third groups of data in Table 42 represent analyses performed also in triplicate on coals processed by the Meyers Process. Two coals processed under different conditions were selected; thus, the extent of pyrite leaching and product sulfate recovery differed in the two experiments. Again, digestion time did not significantly affect sulfur form analysis values. In addition, these data suggest that the Meyers Process product sulfate is as soluble in acids as natural coal sulfate, at least under the conditions of standard ASTM procedure for sulfur forms analyses (the feed coal to Experiments S2 and S4 contained <0.2 wt. percent sulfate; thus, at least part of the sulfate in the processed coals was process-derived).

The last group of data in Table 42 were obtained from analyses on processed coal doped with additional pyrite and iron sulfate. They were principally performed to compare the relative accuracy of ASTM and modified ASTM techniques. However, they also show that digestion time does not affect the accuracy of sulfur form analyses (the analyzed pyritic sulfur values were consistently lower than the computed values indicating that the pyrite doping technique used led to a systematic error--probably due to incomplete incorporation of the pyrite into the coal samples).

In summary, the sulfur analysis investigations performed in this program indicated that the Meyers Process does not affect the accuracy of standard coal sulfur analysis techniques even when recovery of the process sulfur products is incomplete. The conclusion is that carefully performed sulfur analyses should yield the true sulfur forms composition in coal whether processed through the Meyers Process or not. Indirectly, however, by reducing the pyrite concentration of coal to low levels the Meyers Process aggravates the frequently encountered inconsistencies in coal sulfur analyses.

6.2 MEYERS PROCESS MONITORING TECHNIQUES

Functionally, the Meyers Process consists of three major operations: coal pyrite oxidation, reagent regeneration, and product recovery. For every mole of pyrite oxidized in the leaching operation, one mole of coal iron is dissolved into the reagent as Fe^{+2} and 9.2 moles of reagent Fe^{+3} are reduced to Fe^{+2}. Thus, the reagent total iron versus reaction time trace or the ferrous ion versus reaction time trace can be directly translated into coal pyrite concentration versus reaction time information. Either Fe^{+2} or total iron can be used to monitor process performance in the leacher. Preferably the ratio of these iron forms should be used because it is not subject to errors resulting from sample water loss due to vaporization and because the Fe^{+2}/Fe ratio when accompanied by temperature data furnish complete information on all parameters affecting the leaching rate of a given particle size coal. The leaching rate depends on the type of coal and particle size, on temperature, on the pyrite concentration in the coal, and on Y; the Fe^{+2}/Fe ratio is equal to 1-Y. Thus, the monitoring of temperature, Fe^{+2}, and Fe, and knowledge of the pyrite concentration in the feed coal and its particle size furnish the required information to properly monitor the pyrite leaching operation. Temperature and Y are also the appropriate parameters for monitoring the reagent regeneration operation when used in conjunction with oxygen partial pressure monitoring. The sulfur product recovery operations can be easily monitored from the weight of product generated as a function of time with occasional sulfate and elemental sulfur determinations performed to assure the stability of product composition.

Monitoring the Meyers Process by the described techniques presents no problems. The techniques are simple and fast; they require little labor skill and they use inexpensive, commercially available equipment. Weights, temperature, and oxygen partial pressure can be monitored continuously. The total iron and ferrous ion concentrations in the reagent would have to be performed by grab sampling, but the analysis time is short and the reliability high. The ferrous ion analysis performed by the standard ASTM technique requires approximately 10 minutes; the corresponding Fe analysis can be performed in approximately 20 minutes. Several analyses can be performed simultaneously by a single individual. From experience gained from sampling and analysis of several hundred coal slurry samples, it was estimated that the maximum time required from slurry sampling to Y computation is one hour when standard ASTM techniques are used for iron forms analyses. This response time, though adequate, can be reduced to less than 30 minutes if slurry filtration and weighing of the reagent sample are replaced by pipetting the required sample size directly from the slurry and if AA is substituted for Fe titration (see Section 6.1) Guarding against increases in the top size of the coal requires only a single screen which is a part of the coal feed train of the plant.

Monitoring the pyrite concentration in the feed coal and the composition of the product coal could present problems in special situations where quick analysis answers are required. Under normal processing conditions sampling of feed and product coals need not be frequent (once or twice per shift unless there is a more frequent change in coal lots) and immediate analysis data would not be required.

All the elements of the Meyers Process monitoring scheme described above, except product weight sulfate monitoring, have been extensively tested and used at bench-scale. The scheme proved both efficient and reliable. However, its use is predicated on the assumption that the process is totally selective with respect to ferric ion reaction with pyrite and that the coal leaching and reagent regeneration operations are performed separately. Side reactions between reagent iron and coal mineral matter other than pyrite or the organic matrix of the coal will introduce errors in the computation of pyrite concentration in coal from ferrous iron concentration or Y measurements. Experience gained from processing at least 50 different coals by the Meyers Process revealed that for the majority of coals pyrite leaching by ferric sulfate was totally selective within the accuracy of the measurements involved. In cases where excess ferric ion utilization was observed, over that attributable to pyrite oxidation, the excess ferric ions consumed or ferrous ions produced per unit time was the same in different samples of the same coal. Thus, a single determination of excess ferric ion utilization per coal type is sufficient to render the described process monitoring scheme usable with that coal when pyrite leaching is not totally selective.

The described process monitoring scheme becomes inadequate when the chemical desulfurization of coal is performed by L-R processing (simultaneous coal leaching-reagent regeneration). The L-R processing scheme (Section 5) is expected to be used with the high pyrite coals which can not be efficiently desulfurized in coarse sizes. In the L-R scheme the major fraction of the pyrite in coal is removed in the L-R reactor where pyrite leaching and ferric ion regeneration take place simultaneously. Thus, the concentration of the individual iron forms in the slurry are affected simultaneously by both reactions, leaching and regeneration, and the value of Y can no longer serve as a measure of coal pyrite depletion during processing in the L-R reactor (the value of Y can still be used to monitor pyrite depletion in the mixer and ambient pressure reactor of the L-R processing scheme). In order to monitor process performance in the L-R reactor, direct coal sulfur analyses are required either for pyrite or for total sulfur. At least the pyrite content of the coal in the L-R reactor effluent stream must be monitored (the pyrite content of the feed coal to the L-R reactor is attainable from the pyrite concentration in the process feed coal and the delta in the Y values of the mixer).

Examination of time requirements for the generation of coal sulfur data from coal slurries (analysis response time) using conventional sample preparation techniques and standard ASTM analysis methods revealed that such procedure would be totally inadequate for monitoring the L-R reactor. The response time would be several hours long with sample preparation being the major time consumer. Sample preparation entails slurry filtration, coal washing, coal drying, and coal sampling and weighing; coal grinding may also be necessary. Coal drying requires a minimum of four hours, if performed according to acceptable ASTM procedures; the remaining operations require a minimum of one hour. The minimum time required for the performance of the standard ASTM pyrite analysis is 2 hours; a total sulfur analysis by Eschka could be performable in 1 hour. Thus, the minimum response time for total sulfur data is 6 hours and for pyritic sulfur data 7 hours. Such response time was considered too long to serve as the means of obtaining process performance information which would permit timely changes in process parameters to correct processing deficiencies and prevent the generation of a final coal product with a sulfur content higher than desired. This conclusion is valid even though slurry residence time in the ambient pressure reactor, in series with the L-R reactor, could be as long as 40 hours, because the ambient pressure reactor will not normally have the flexibility of affecting large changes in pyrite leaching rates.

After careful examination of the sample preparation procedure, it was decided that it could be shortened considerably, with less than 10 percent potential penalty in the accuracy of the analysis, if coal washing and coal drying were eliminated. In the case of pyrite analysis, the elimination of these two operations affects only the accuracy of the weight of the sample subjected to analysis. Data from over one hundred coal slurry filtrations revealed that the quantity of reagent remaining on the coal did not vary by more than ± 5 percent of the weight of dry coal, even if no effort was made to exactly reproduce filtration times; in the majority of experiments the deviation was less than ± 3 percent. Thus, sample preparation time was reduced to approximately 0.5 hours and the response time for pyrite analysis using the standard ASTM technique (ASTM D-2492) to approximately 2.5 hours. This response time was reduced to approximately 2 hours when the iron determinations in the hydrochloric and nitric acid extracts were performed by AA instead of titrimetric procedures (see Section 6.1). A two hour response time was considered adequate for monitoring the L-R reactor.

The analysis response time could be reduced to approximately 1 hour, if total sulfur rather than pyritic sulfur is used as the means of monitoring pyrite depletion in the L-R reactor. However, the accuracy of the data may be appreciably lower than that obtainable with the shortened pyrite analysis procedure described above. The total sulfur analysis procedure utilizes the Leco sulfur analysis technique, but on wet coal. The data presented in Section 6.1 showed that the Leco technique furnishes high accuracy sulfur values when the sulfur concentration in coal (dry) is less than 3 wt. percent and that its accuracy is not affected if a portion of the sulfur in coal is in the elemental form. However, similar sulfur accuracy determinations were not performed with wet coal, though no problems are anticipated. The potential source of error is associated with the fact that the determined sulfur value must be corrected for the product elemental sulfur, which was not recovered prior to analysis, and for the reagent sulfate on the wet coal (the coal sample may be washed prior to analysis, but then the response time increases to approximately 1.5 hours). The sulfate correction can be made from the estimated weight of reagent solution on the coal and the Fe concentration and Y values determined routinely as elements of the process monitoring scheme described earlier in this report section. Assuming that 40 percent of the reacted pyritic sulfur converts to elemental sulfur, a valid assumption based on data generated to date from several coals, the determined depletion in total sulfur by the described procedure represents 60 percent of the leached pyrite during the reaction time interval examined. The feasibility of this procedure was not tested experimentally in an integrated form.

In parallel with the above investigations, a literature search was undertaken aiming at the identification of novel, rapid procedures for pyrite determination in coal. The chemical abstracts were searched for the last decade with limited success. Three insufficiently developed new pyrite analysis techniques were discovered, but with no demonstrated potential to serve as monitoring techniques for the Meyers Process.

One of these techniques was the result of a feasibility study performed by Barringer Research in Ontario, Canada under government contract in 1968;[12] it involves the sensing of sulfides in coal by a microwave detection system. Though an interesting approach because it permits the determination of pyrite in the coal without leaching, the data on the technique is insufficient to evaluate its accuracy.

A second technique developed and used by the Illinois State Geological Survey Institute is a lithium aluminum hydride reduction procedure for pyrite in coal.[13] This technique is affected by the presence of elemental sulfur in the coal (positive interference) and, therefore, it is not better than a total sulfur analysis technique (Leco or Eschka) for monitoring the Meyers Process performance. In fact, it is more complicated and less tested.

The third technique is a soft X-ray procedure developed at Pennsylvania State University.[14] It is reportedly capable of determining the concentration of pyritic, sulfate, and organic sulfur in coal using measurements of X-ray fluorescence from four discrete wavelengths. This promising procedure is a very recent development-first reported in December 1974- and therefore inadequately tested. Attempts in our laboratory to duplicate the reported data using a pentaerythritol analyzing crystal and an XRD-5 spectrophotometer were not successful because this system was incapable of resolving the sulfur K_B doublet on which the procedure is based. Personal contact with Dr. Eugene White at Penn State University (co-author of the paper) revealed that the instrument they used had to be specially modified to obtain the desired resolution and the surface temperature of the crystal (Germanimum) had to be regulated within ± 0.1°C to maintain dispersion stability. At the present time, the procedure though potentially viable, would require extensive instrument and procedure development before being amenable to use as a process monitoring technique. However, X-ray fluoresence is an attractive analytical technique because it is potentially capable of being used to analyze more than one element and because it is amenable to automation. Its drawback, as a monitoring technique involving coal slurries, is that it requires that the coal be dried prior to analysis and coal drying is a time-consuming operation.

7. MATERIALS COMPATIBILITY

Static testing of common stainless steel alloys in an environment simulating that of the Meyers Process but with low solution oxygen concentration revealed that many stainless materials had severe corrosion problems. However, dynamic testing in the L-R apparatus under actual processing conditions indicated a much wider range of stainless material stability to corrosion.

The following composition and operating conditions are typical for the Meyers desulfurization process:

$Fe_2(SO_4)_3$ approximately 18%

H_2SO_4 approximately 10-20%

$FeSO_4$ approximately 1%

Finely dispersed O_2

Possibly chloride contamination

Temperature 275°F, Pressure 50-100 psi

Agitation and vigorous O_2 bubbling

Coal abrasive charge

Obviously, materials to be used for the construction of the desulfurization process plant must possess the necessary mechanical strength, abrasion resistance and corrosion resistance properties. Of course, design life, material cost, safety and maintenance are factors for tradeoff consideration with material performance.

Specific data on corrosion rates under the conditions of the leaching process considered here are unavailable from literature. It is recognized that in view of the complexities of the electrochemical processes associated with corrosion, published data on corrosion tests under similar environments may not be directly applicable. No assumptions or extrapolations of available data may be possible. Corrosion rates have to be determined experimentally under the specific conditions of the process in consideration. However, there is adequate understanding and published data on corrosion to limit the choice to certain classes of materials.

An initial literature survey and alloy selection discussion, the results of static testing for screening of applicable materials and experimentation on materials behavior in the bench-scale reactor under dynamic conditions are presented in the three sections to follow.

7.1 LITERATURE SURVEY AND ALLOY SELECTION CRITERIA

Discussion of Alloy Composition and Corrosion Mechanisms

In terms of the more common types of corrosion, the desirable metal composition and metallurgical structure are discussed below.

Corrosion

In the baseline Meyers Process design the physical size of the welded assemblies may be such that it may not be convenient or practicable to solution anneal or carry out other post-welding metallurgical heat treatment of the finished structure. Hence, the material chosen must resist sensitization (preferred precipitation of chromium carbide in the grain boundaries). Alloys containing low C and/or some Nb, Ta are required to avoid a sensitized condition which is highly susceptible to intergranular corrosion.

Chloride ions present in small concentrations in water, and probably also in the coal charge, may penetrate passivating films and initiate pitting corrosion. The critical temperature at which pitting attack is appreciable increases with increased Mo content. At an operational temperature of $275^{\circ}F$, a high Mo content is desirable. Mo is the commonly used alloying element to impart resistance to pitting corrosion.

Near boiling temperatures, H_2SO_4 between 20-80% acid concentration causes serious attack on most stainless steels. Addition of ferric sulfate, $CuSO_4$ or O_2 reduces this attack greatly. Alloys containing Mo, Co/Si + high level of Ni show good corrosion resistance in these environments.

Chloride ions, although present in small concentrations, would cause severe stress-corrosion cracking in the presence of welding and mechanical stresses and the tensile stresses in a pressure vessel. Abrasive grains may also cause notches that initiate Griffith crack propagation. A high level of Ni provides good resistance to chloride ion stress corrosion cracking.

High Ni + Cr and a high Mo content are useful in the presence of hot oxidizing ferric salt solutions of fluctuating concentrations.

Differential aeration or oxygen concentration initiates corrosion in crevices. Hence, good agitation and dispersion of O_2 bubbles in practice would not only improve the sulfur leaching process but also reduce corrosion.

Stainless Steels, Coatings and Inhibitors

The advantages of Mn-Ni substitution in austenitic stainless steels are increased resistance to stress corrosion, carbide precipitation (hence sensitization) and pitting corrosion. These alloys are further improved by addition of Mo to provide increased resistance against pitting corrosion and Nb-Ta for increased stabilization against sensitization. One such alloy is Armco 22-13-5 containing 5% Mn with additional Mo and Nb. The Carpenter 20Cb-3 is also a similar alloy but with a low Mn content.

Armco 22-13-5 (Nitronic-50) austenitic stainless steel is superior to 316 or 316L in corrosion resistance and costs more than 316L. It also combines high strength with corrosion resistance and can be useful in stressed parts such as pumps, valves, screens and wire supports.

Table 43 compares the corrosion rates of Armco 22-13-5 with 316 and 316L in different corrosive media.

TABLE 43. COMPARISON OF CORROSION RATES OF ARMCO AND 316/316L STEELS

Test Medium	Armco 22-13-5	316/316L
10% $FeCl_3$, Amb. Temp.	<0.001 gm/in_2, no pits	0.0112 gm/in^2 pitted
10% H_2SO_4, boiling	0.356 Ipy (in per year)	0.73 Ipy
20% H_2SO_4, boiling	1.64 Ipy	2.2 Ipy
Nitric acid test	0.0072 Ipy	
Ferric sulfate + Sulfuric acid	0.0108 Ipy	

This alloy is recommended for stressed parts and if chloride ion stress corrosion cracking or intergranular corrosion is a problem with conventional 300 series stainless steel alloys.

Types 347 (Nb + Ta), 321 (Ti), 309 Cb, and 310 Nb are stabilized steels which can be used in the as-welded condition. Data on their corrosion properties in H_2SO_4 - $Fe_2(SO_4)_3$ are not readily available.

Organic inhibitors used in pickling tanks may be useful in minimizing corrosion problems. Some examples are thiourea, dibutyl sulfoxide, amines, O-polythiorea, quinoline derivatives, ketones, etc. Proteins such as milk albumin are useful in providing a protective film. Also 0.2% AS in H_2SO_4 greatly reduces corrosion. These may be considered if they do not adversely affect the leaching process.

Teflon or Kynar (polyvynilidene fluoride) coatings, may provide additional protection in view of the fluctuating corrosion conditions. Kynar can be coated inside small tubings. Tough, uniform teflon coatings are possible to apply on large tubings and inside reaction vessels. Sleeving with thin-walled teflon tubing is also a possibility. Teflon is completely stable in boiling H_2SO_4 and $Fe_2(SO_4)_3$ solutions and Kynar is also stable to a high degree.

Survey of Literature Data on Corrosion

Tables 44 and 45 summarize available data on materials for conditions somewhat similar to those under consideration. A comparison of these data with the results of the tests conducted in this study (Table 48, page) indicated the importance of generating corrosion data under specific conditions.

TABLE 44. CORROSION DATA FROM LITERATURE ON 304 AND 316SS[15]

				Corrosion Rate, Ipy*		
Ferrous sulfate	H_2SO_4	Ferric sulfate	Temp	Time	304	316
-	150 ppm	603 ppm	-	61 days	0.017	<0.0001
-	270 ppm	9424 ppm	-	61 days	<0.0001	<0.0001
Mostly	With free acid (pH=1)	-	100°F	67 days	0.0005	0.0004
	6% free acid	1.5%	160°F	7 days	<0.0001	-

*Inches per year

7.2 EXPERIMENTAL CORROSION STATIC TEST PROGRAM

7.2.1 Experimental Method

Figure 35 shows the stainless steel bomb assembly used to carry out the static corrosion test under simulated plant conditions. Four 1-1/2" sections of 1/2" O.D. tubings of different candidate materials were welded together using the TIG process without filler rods as seen in Figure 36. This served as a support for the sheet candidate materials to be tested, which were machined into flat tensile test coupons after welding in pairs. Thirty-two specimens were assembled to the configuration shown in Figure 37. The coupons were held in radial slots on the periphery of teflon support rings fixed to the tube with 304 S.S. screws. All the test coupons were machined flat and polished with 3/0 emery paper (∿10 μ-inch finish) and were used in the polished condition after welding with

TABLE 45. CORROSION DATA FROM LITERATURE ON VARIOUS ALLOYS[15,16,17,18]

Corrosive Medium	Temp F°	Time Days	Aeration	Agitation	Average Corrosion Rate (ipy)*					
									Hastelloy C-4	
					Type 304	Type 316	Incoloy 825	Inconel 625	Un-Welded	As welded
(1) $FeSO_4$, H_2SO_4 PH=1	100	67	X	X	0.0005	0.0004	--	--		
(2) 50% H_2SO_4 42 g/l $Fe_2(SO_4)_3$	Boiling	1	--	--				0.070	0.111	0.114
(3) 1.5% Ferric Sulfate +4% Free Acid	160	31	--	X	.0001	.0001	--	--	--	--
(4) 15% H_2SO_4	176	--	--	--	--	--		0.007		
(5) 15% H_2SO_4	104	1			0.03	nil	--	--	--	--
(6) 80% H_2SO_4	176	--	--	--	--	--	--	0.090	--	--
(7) Stress Corrosion Test 42% $MgCl_2$ Soln	Boiling	1000 hrs.	--	--	--	--	--	--	--	No Cracks
(8) 4% Ferrous Sulfate Ferric Sulfate H_2SO_4 PH 2.5	162	27	X	X	0.017	0.0006	--	--	--	--
(9) 60% Solids g/l 28-55 gm/R H_2SO_4 5-10 g/l Fe+++ Some ferrous 0.1% $NaClO_3$	113	41					.0001			--

*Inches per year

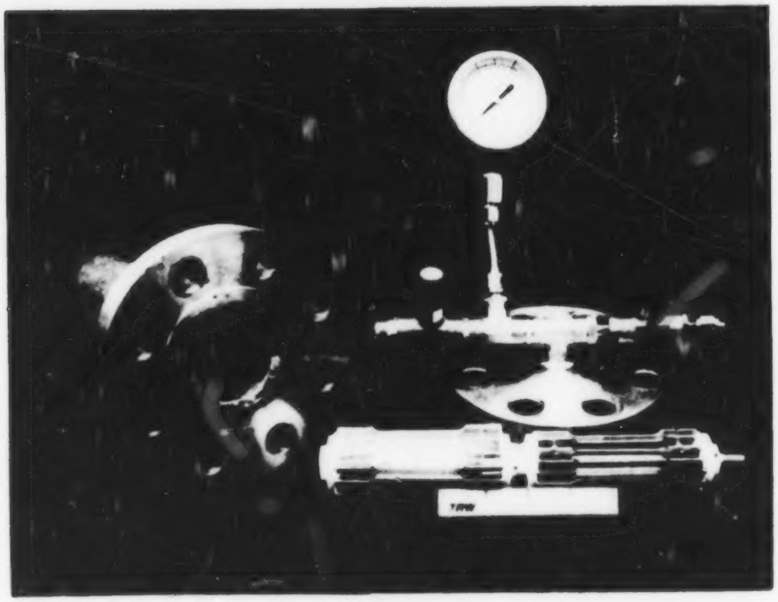


Figure 35. Bomb Test Assembly

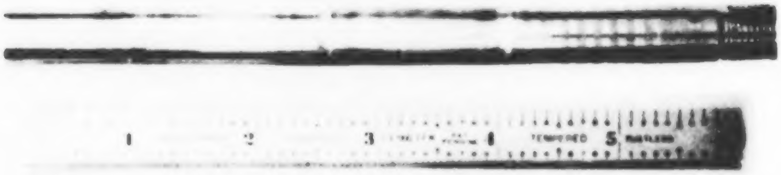

1
2
3
4
TEMPERED
5

Figure 36. Composite Welded Tube Used In Test. From Left to Right 304, 304L, Armco and 316L

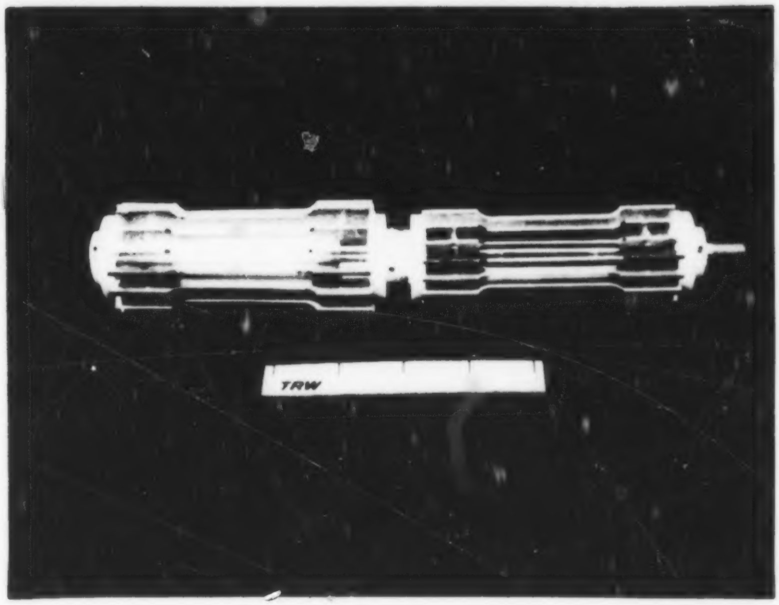


Figure 37. Test Coupon Stack: 32 Tensile Coupons Assembled Around The Central Welded Tube With Teflon Support Rings

no special annealing heat treatment. The tubes were also used in the as-welded condition. All test coupons were carefully weighed and sized prior to loading in the bomb.

The bomb was filled with ferric sulfate leaching solution used in the process. The flanges were bolted together with a high temperature gasket seal. The valve fitting on the outside of the top flange enabled the bomb to be pressurized with O_2. Heating tape was used to attain the temperature.

Table 46 lists the materials and conditions used in the test.

7.2.2 Initial Runs and Modifications

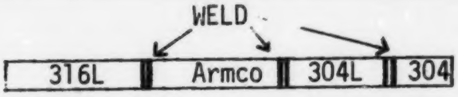
A chromel-alumel thermocouple (TC) encased in a 304 S.S. protective tube was used initially and the TC being immersed in the corrosive solution with the aid of a T-fitting on the flange. After only 16 hours of testing, the bomb had to be disassembled because the thermocouple sheathing (304 S.S.) was completely corroded away. The 304 S.S. screws used to hold the teflon rings showed signs of corrosion. The bomb was cleaned and reassembled without the TC which was now placed on the outer bomb wall. The gradient across the S.S. wall of the bomb was assumed to be negligible.

After 300 hours of testing at temperature and pressure, the bomb was disassembled for replacement of the gasket. It was found that the bomb interior and test coupon stacks were covered by a heavy brown deposit, and the 304 S.S. screws that were used to keep the teflon support rings in position were very severely corroded, with some so completely reacted on that they crumbled to a powder on touching. The coupons themselves showed no signs of corrosion. The stressed contact points between S.S. screws and the metal tubing were also pitted.

For further continuation of the test, the 304 screws were replaced and new solution was used. The test coupons and bomb were cleaned of all deposits. The bomb was heated for a second period of 700 hours (solution exchange at 300 hours should not have had a material impact on the test).

TABLE 46. LIST OF MATERIALS TESTED

Composite Support Tube (welded)



	Welded Metal Pairs	# Samples
Tensile Test Coupons:	304 - 304	2
	316 - 316	3
	316L - 316L	3
	347 - 347	2
	321 - 321	2
	Armco - Armco	2
	Carp - Carp	2
	Inconel - Inconel	1
	Incoloy - Incoloy	1
	316 - 304	2
	316L - 304	2
	Armco - 316	1
	Armco - 316L	1
	Incoloy - Armco	1
	Carp - 316	1
	Carp - 316L	1
	321 - 316L	1
	321 - 316	1
	347 - 316	1
	347 - 316L	1
	347 - 304	1

Temperature	*260°F
Pressure	100 psig
Time	1000 hours (300 hours - first run + 700 hours - second run)

* A temperature excursion to 320°F for an unknown time between 24 and 60 hours occurred during the course of the test initially

At the end of the second period of exposure for 700 hours (total of 1000 hours on the test coupons) it was observed that the bomb and the samples were covered by a very heavy brown to blackish-brown deposit. Part of the 304L portion of the composite tube between the weld areas 304/304L and 304L/Armco was completely corroded away as shown in Figure 38. The heavy deposit is partly from the corrosion products and partly also from the solution, which was now dark green in color, with the total iron content down by 44% and nearly all ferrous. The change in solution characteristics is shown in Table 47.

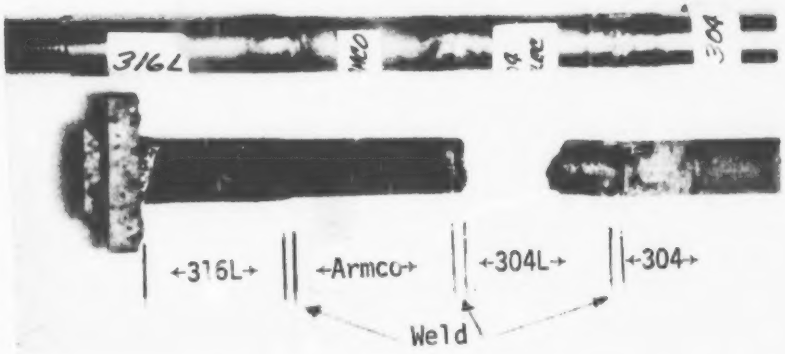
TABLE 47. FERRIC SULFATE CORROSIVE MEDIUM

	Initial (mg/g)	300 hrs.	700 hrs.
Total Fe	50	46	28.4
Fe^{++}	13	21	28.1
Brown heavy deposit	None	Considerable	Very heavy
Color	Brown	Green	Darker Green
Cr/Ni SO_4 and Cl - ions	- NOT ANALYZED -		

In order to obtain weight losses, the tough adhering deposits had to be removed. The procedure used was as follows. The heavier buildups were removed by mechanical brushing with a nylon brush and acetone in an ultrasonic bath. Some of the more adherent deposits were loosened by thermal cycling between 100°C and 0°C. The samples weighed after the mechanical removal still showed a weight gain as compared to the original, indicating incomplete removal of the oxide deposits. Hence the following pickling procedure was used:

a) 60 minute dip in 20% NaOH + 5% $KMnO_4$ at 200°F

b) 10 to 30 seconds in 15% H_2SO_4 at 180°F



≈ 2/3X

Figure 38. Comparison of Corroded And Control Tubes.

BOTTOM: Tube After 1000 Hours Exposure to Corrosive Environment. NOTE: 304L Tube Disintegration

TOP: Control Tube: The tubes have been aligned such that weld zones are one below the other. The missing portion (≈ 1 inch of 304L) of the exposed tube has been corroded away. From left to right, the sections are 316L, Armco, 304L, and 304. The threaded portion at the left end of the exposed tube was cut off before the test. The teflon support ring is seen on the left.

This procedure removed the oxide deposit effectively without attacking the bare metal. Type 316 S.S. was attacked somewhat by the H_2SO_4 solution. A set of control samples was also subjected to identical treatments in order to correct for weight loss from the bare metal due to the pickling procedure. Since the oxide deposits on the coupons could only have inhibited the reaction of the pickling bath on the metal substrate, the weight losses obtained after correction must represent a minimum figure. However, the corrections are small and this effect is not likely to be appreciable.

7.2.3 Results and Conclusions of the Bomb Test

The corrosion rates are calculated from the weight loss and surface area and density for each coupon in units of milligram (loss) per square decimeter (mdd) per day. This can be converted to the more conventional inches penetration per year units (ipy) using the factor mdd x $\frac{(0.001437)}{d}$ = ipy where d - density (gms/cc). The corrosion rates were found to vary by a factor of three in duplicate samples of the same material. This large variation is due to the position of the sample in the bomb stack and the degree of protection from additional corrosion afforded by the accumulation of the surface deposits. But the differences between two types of materials is marked. It should be emphasized that due to the static conditions in the bomb, the corrosion rates obtained are probably lower than for the actual dynamic conditions and are more meaningful as relative figures than as absolute corrosion rates.

Table 48 gives a summary of the corrosion rates, visual appearance and tensile test results obtained.

Several metallographic mounts were prepared from the test and control samples to study the extent of corrosion and the corrosion mechanism. Mounts were made from near the weld zone as well as near each end of the grip section. Figures 39 and 40 show the microstructure of the exposed (corrosion tested) 304 S.S. coupons and Figure 41 shows the microstructure of a 304 S.S. control sample. It was observed that while sensitization

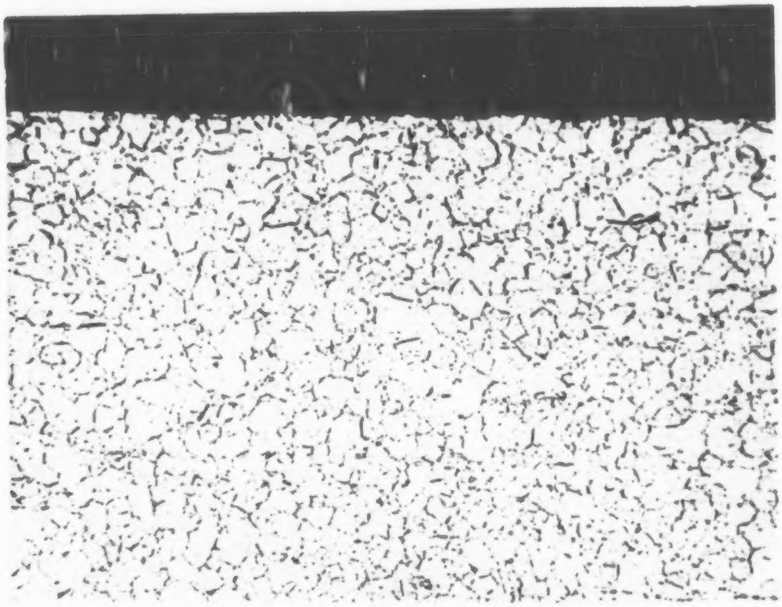
TABLE 48. COMPILATION - COAL CORROSION MATERIAL EVALUATION

SUBJECTED SPECIMENS										CONTROLS								Corrosion Rate	RATINGS			
Specimen Number	Matl.	Y.S.	UTS	Elong.	Break	Defect	Visual	Wt.Loss	Gm/Cm^3 Density	Spec. No.	Matl.	Y.S.	UTS	Elong.	Break	Polish	Etch	ipy	Corrosion Rate	Mech Prop Δ	Edge Cracking (Metallographic)	Visual
1A	304/304	44.7	92.4	40	W	Few sml voids	Poor	0.0680	7.89	1A	304	48.4	92.7	42	W		✓	0.0014	5	A	1	9
1B	304/304	44.4	92.5	40	W	O.K.	Poor	0.0510	7.91	1B	304	44.1	92.2	37	W	✓	✓	0.0010				
2A	316/316	35.7	78.4	43	316	Few sml voids outside welds	Poor	0.1189	7.98	2A	316	42.3	80.0	31	W		✓	0.0024	8	B	10	8
2B	316/316	36.0	74.6	34	316	O.K.	Poor	0.3783	7.95	2B	316	39.9	84.7	52	W	✓	✓	0.0075				
2C	316/316	36.5	64.7	15	316	Few sml voids outside welds	Poor	0.3934	7.98	2C	316	40.7	78.5	30	W	✓		0.0079				
3A	316L/316L	44.4	79.8	26	W	O.K.	Good	0.2477	7.99	3A	316L	44.1	81.4	30	W		✓	0.0049	7	A	4	6
3B	316L/316L	44.6	78.5	25	W	O.K.	Good	0.3432	8.03	3B	316L	49.0	83.9	23	W	✓	✓	0.0068				
3C	316L/316L	47.6	84.0	27	W	O.K.	V.Good	0.0832	7.91	3C	316L	44.3	80.4	24	W	✓		0.0017				
4A	347/347	43.0	68.2	35	W	Couple voids at weld	Poor	0.1889	7.93	4	347	44.7	73.8	15	W	✓	✓	0.0037	9	?	3	7
4B	347/347	41.0	70.0	24	347	Few sml voids outside welds	Poor	0.4019	7.93									0.0080				
5A	321/321	65.0	88.4	23	W	Small spot at weld	Good	0.1665	7.91	5	321	45.5	90.4	31	W	✓	✓	0.0034	6	A	1	5
5B	321/321	43.1	68.2	26	321	Small speck at weld	V.Good	0.0632	7.86									0.0014				
6A	ARM/ARM	58.0	100.2	23	W	Nothing of sig.	V.Good	0.0056	7.92	6	Armco	56.6	103.9	26	W	✓	✓	0.0001	4	A	1	3
6B	ARM/ARM	62.2	99.1	21	W	O.K.	V.Good	Not Used	7.91													
7A	CARP/CARP	56.5	94.2	20	W	Small voids large @ weld	V.Good	0.0127	8.07	7	Carp	50.4	92.5	21	W	✓	✓	0.0002	2	A	1	4
7B	CARP/CARP	56.6	96.3	23	W	O.K.	V.Good	0.0022	8.04									-				
8	INCONEL/ INCONEL	74.5	117.7	18	W	Various voids large @ weld	V.Good	0.0170	8.46	8	Inconel	74.2	123.9	22	W		✓	0.0003	3	A	1	2
9	INCOLOY/ INCOLOY	56.7	91.8	15	W	O.K.	V.Good	0.0072	8.16	9	Incoloy	48.1	86.1	17	W	✓	✓	0.0001	1	A	1	1
10A	316/304	39.2	77.4	35	316	O.K.	Poor	0.2974	7.92	10	316/304	42.4	84.5	35	W	✓	✓	0.0059				
10B	316/304	39.0	79.4	41	316	O.K.	V.Poor	0.2399	7.95									0.0048				
11A	316L/304	46.4	87.4	34	W	O.K.	Fair	0.0630	7.94	11	316L/304	47.7	87.0	30	W	✓	✓	0.0013				
11B	316L/304	46.9	90.2	36	W	Numerous voids at weld	Fair	0.0576	7.94									0.0011				
12	ARM/316	40.2	78.8	32	316	Large void at weld	Fair	0.1649	7.95	12	ARM/316	43.7	85.2	53	316	✓	✓	0.0032				
13	ARM/316L	49.4	89.6	31	W	Couple voids outside weld	Good	0.0190	7.95	13	ARM/316L	49.6	89.2	28	W	✓	✓	0.0004				
14	INCOLOY/ ARM	56.1	95.6	23	W	Couple sml. voids.out.wld.	V.Good	0.0014	8.04	14	INCOLOY/ ARM	52.8	93.2	20	W	✓	✓	-				
15	CARP/316	39.0	73.9	34	316	Small abt.weld	Poor	0.1965	8.00	15	CARP/316	42.3	76.9	16	W	✓	✓	0.0039				
16	CARP/316L	51.0	83.6	29	W	O.K	V.Good	0.0105	8.00	16	CARP/316L	49.1	89.5	31	W	✓	✓	0.0002				
17	321/316L	44.6	82.8	25	W	O.K.	Fair	0.0975	7.99	17	321/316L	41.7	80.6	18	W	✓	✓	0.0020				
18	321/316	35.8	65.3	22	321	O.K.	Poor	0.4524	7.92	18	321/316	42.5	83.2	28	W	✓	✓	0.0095				
19	347/316	39.0	80.0	30	W	O.K.	V.Poor	0.3346	7.96	19	347/316	40.8	82.5	34	W	✓	✓	0.0066				
20	347/316L	45.3	76.7	20	W	O.K.	Fair	0.0833	7.96	20	347/316L	40.7	78.0	24	W	✓	✓	0.0017				
21	347/304	45.1	88.6	40	347	O.K.	Poor	0.2921	7.92	21	347/304	45.0	92.1	38	W	✓	✓	0.0060				

Rating Codes:
1 = best, largest number = worst

A = No apparent change

B = Slight change



200X

Figure 39. Microstructure of 304 Test Coupon After 1000 Hours Exposure

400X

Figure 40. Microstructure of 304 Test Coupon at 400X Showing Sensitization at Grain Boundaries

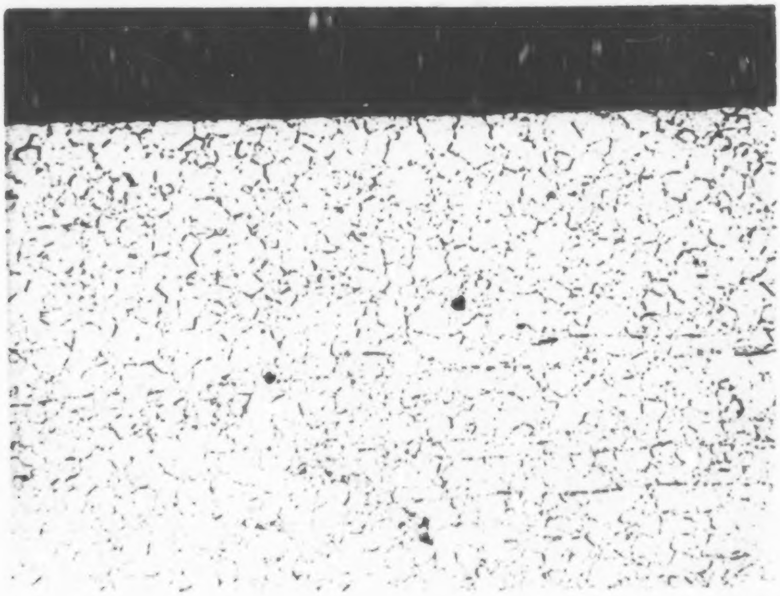


Figure 41. Microstructure of Unexposed Sample of 304 Test Coupon

had indeed occurred at some distance from the weld zone, intergranular corrosive attack was barely evident. Pitting corrosion was not seen here.

Figures 42, 43 and 44 show that very severe pitting corrosion occurred just outside the weld area in 316. Both large and small pits were observed, and some of the large corroded areas were considerable in size.

Figures 45 and 46 show the edges of the mounted specimens of a control and exposed sample of 316. Cracks near the outer edge due to an embrittling effect of the corrosion are evident in Figure 46. Figures 47 and 48 similarly show the edges of a corroded and exposed sample of 316L. Cracking and pitting due to corrosion are evident.

Figures 49 and 50 show cracked and exposed edges of 347. Other areas of corroded 347 showed evidence of pitting similar to 316 though not quite as extensive.

Figures 51 and 52 show areas of Incoloy 825 in the unexposed and exposed conditions. There is evidence of either cracking or corrosion.

Figures 53 and 54 show the unexposed and exposed areas near the weld of the 304L/304 joint. It is recalled that the 304L tube near the weld was so severely attacked that part of the tube fell apart as seen in Figure 38. Figure 55 shows the corroded area on 304 tube. Figure 56 shows the corroded inner-edge of the 304L tubing. Figure 57 shows the weld and parts of 316L and Armco tubing. Severe pitting exists on 316L with much less on the Armco tubing.

Figure 58 shows the uncovered (top) portion of the 316L tubing and bottom portion which was covered tightly with teflon tape. The much more severe pitting in the unprotected area is evident.

Figure 59 shows cracks in the I.D. of Armco tube while the O.D. Figure 60 shows only pits. Figures 61 and 62 shows, respectively, the O.D. and I.D. of the exposed 316L tubing.

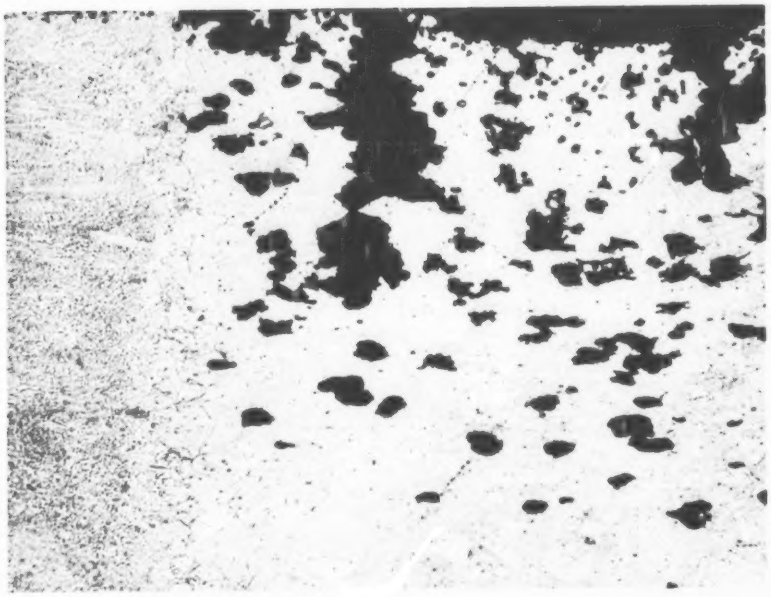


Figure 42. Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure

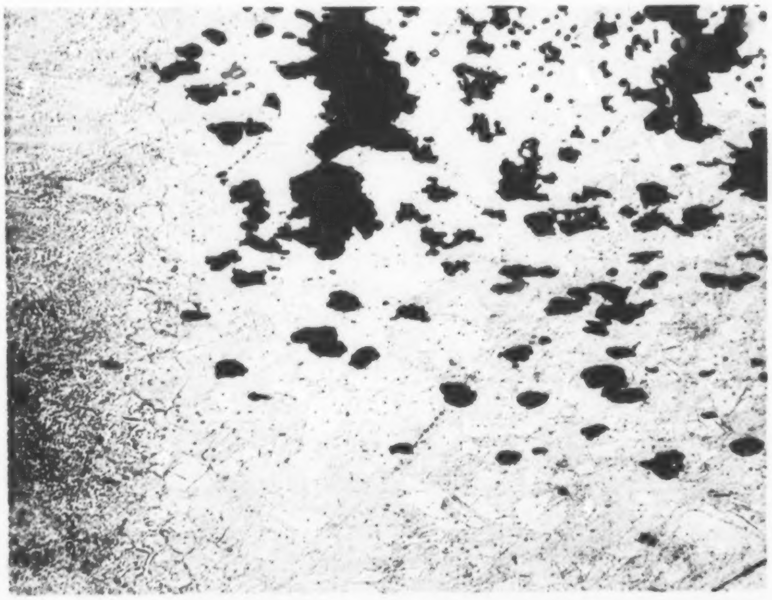
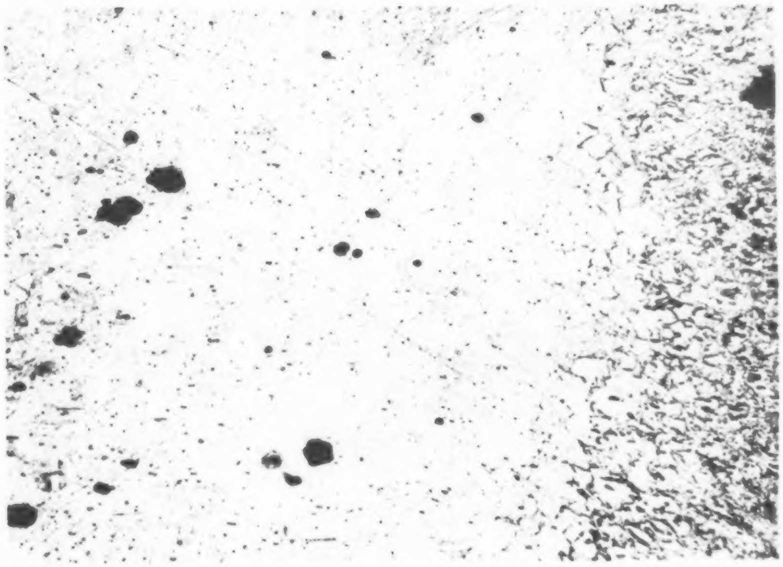


Figure 43. Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure



100X

Figure 44. Micrograph at 100X Showing Very Extensive Pitting Type of Corrosion Just Outside the Weld Zone in 316SS After Exposure

200X

Figure 45. Edge of 316 Control Sample Showing Elongated Stringers Due to the Tensile Test

200X

Figure 46. Edge of Exposed Test Coupon of 316 Showing Transgranular Cracks Extending Inward From Cut Edge

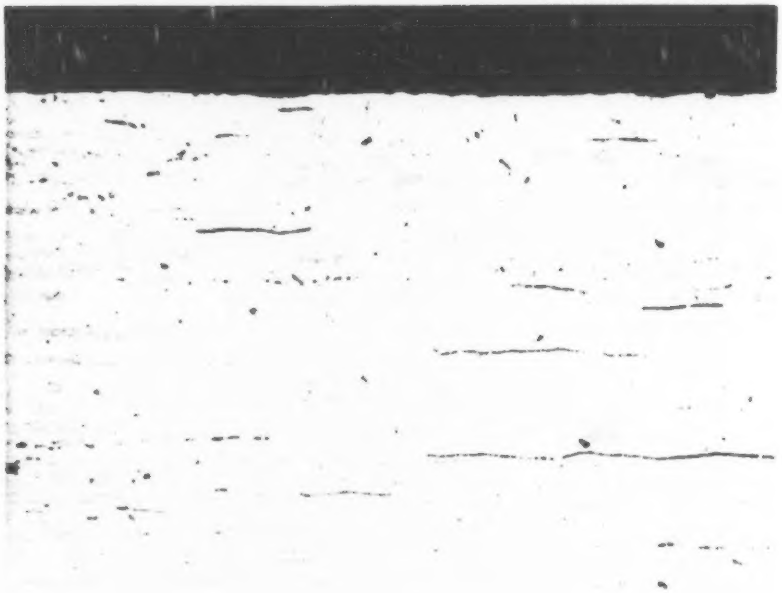
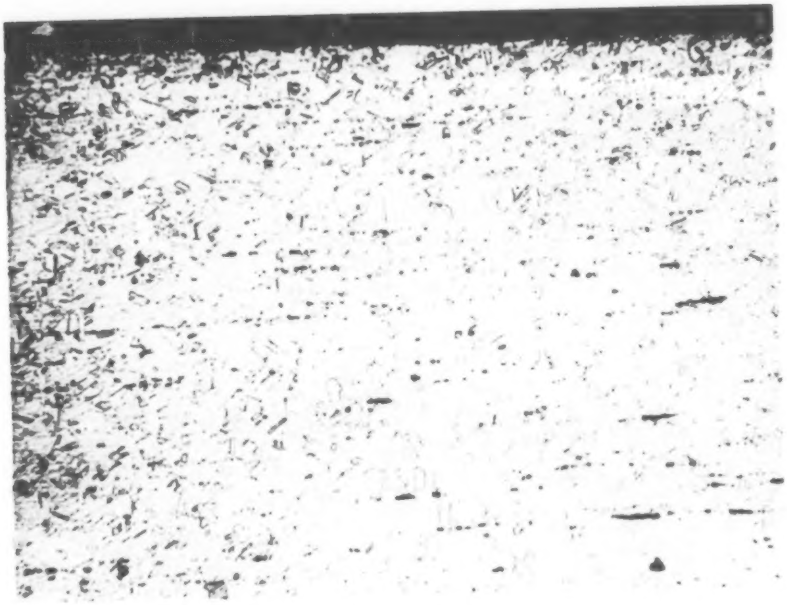


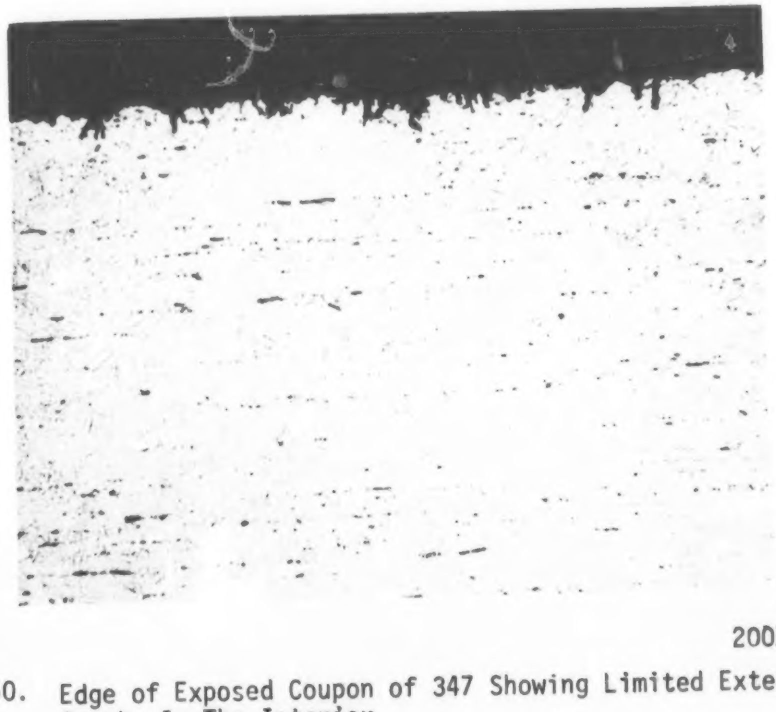
Figure 47. Edge of 316L Control

Figure 48. Edge of Exposed 316L Showing Crack Extension Along Crack Sensitive Corroded Paths and Pitting



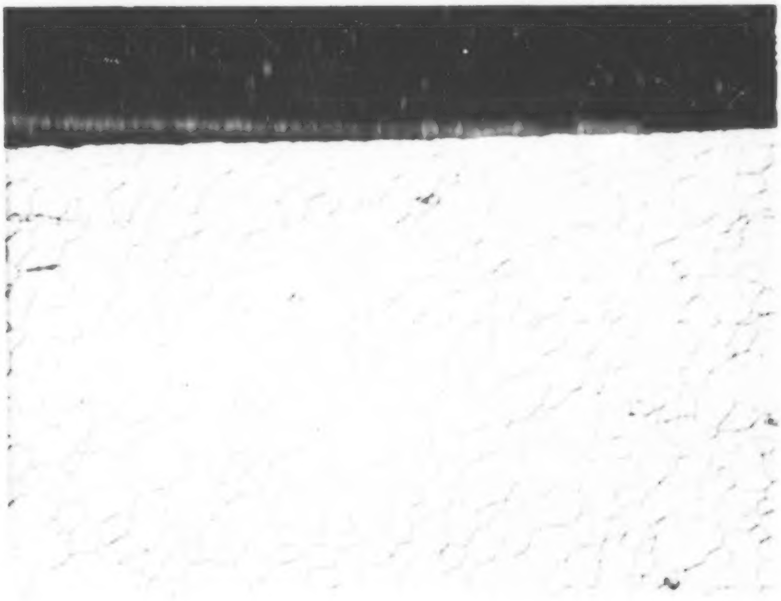
200X

Figure 49. Edge of 347 Control



200X

Figure 50. Edge of Exposed Coupon of 347 Showing Limited Extension of Cracks In The Interior



400X

Figure 51. Edge of Incoloy 825 Control

400X

Figure 52. Edge Of Exposed Incoloy 825 Test Coupon

304L
Parent
Metal
200X

Figure 53. Weld Between 304 And 304L In The Control Tube Sample

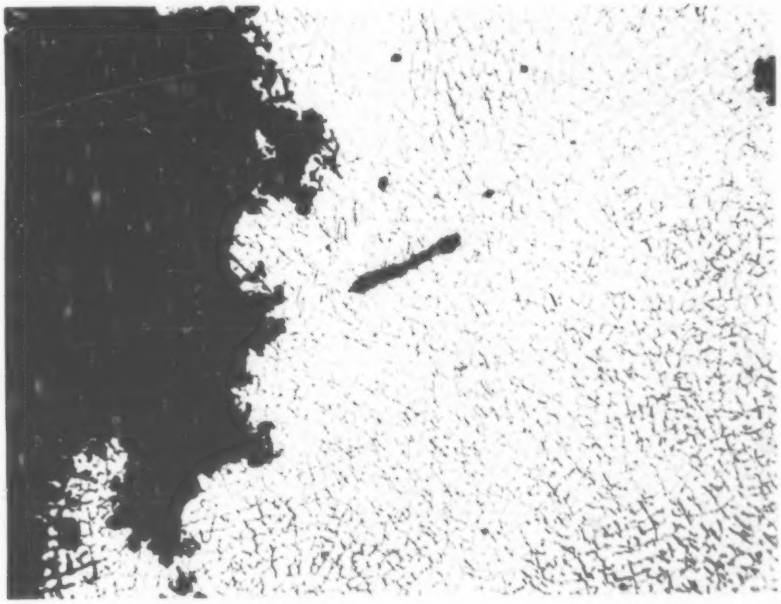
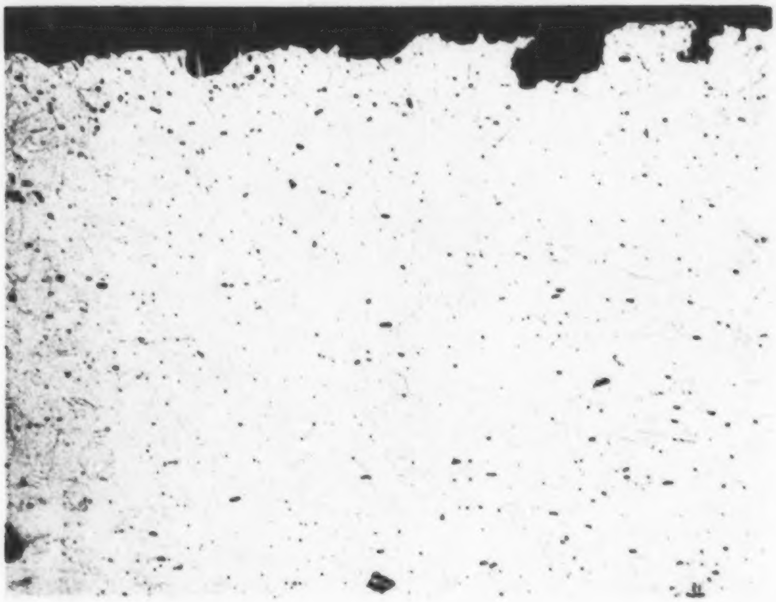
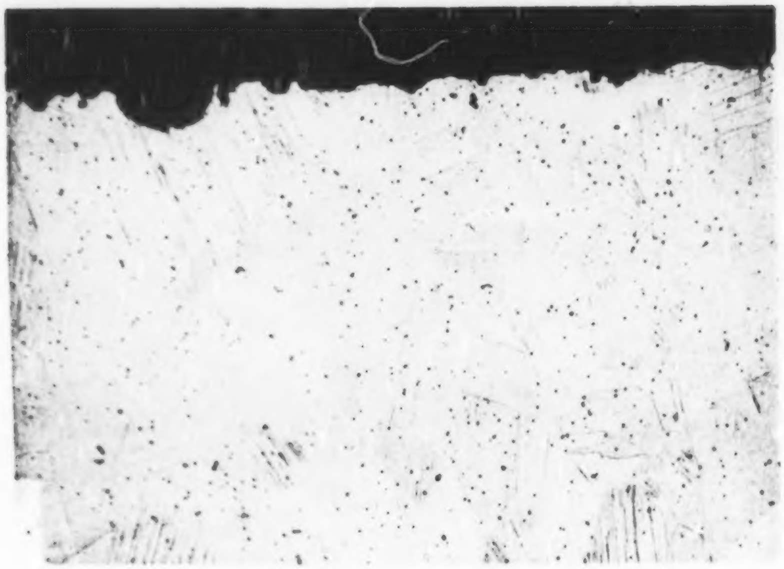


Figure 54. Weld Between 304 and 304L Tubes Showing Severe Corrosion Effects After Exposure



200X

Figure 55. Outer Diameter of 304 Tube After Exposure Showing Corrosion Along The Edge And Pits On Surface



200X

Figure 56. Inner Edge Of Exposed 304L Tubing Showing Corroded Areas

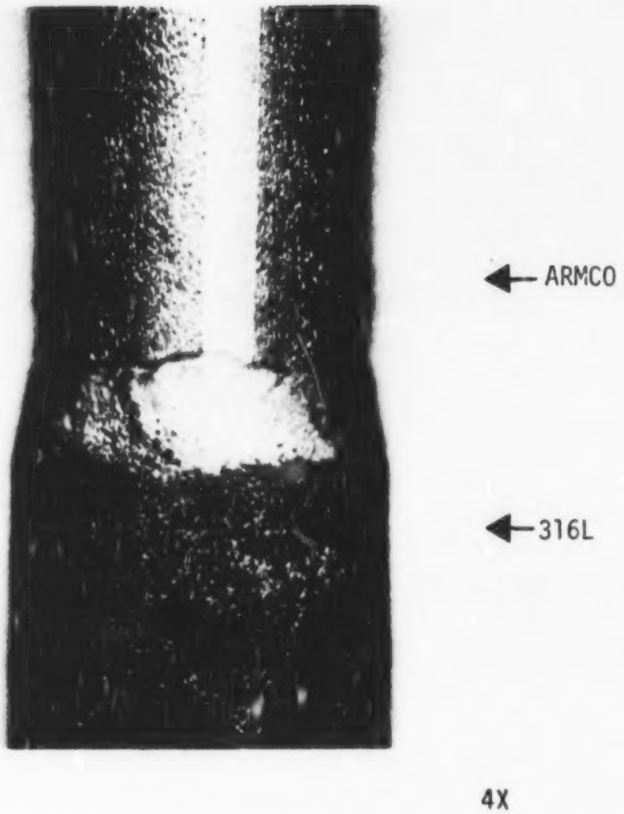

ARMCO
316L
4X

Figure 57. Exposed Tube Sample

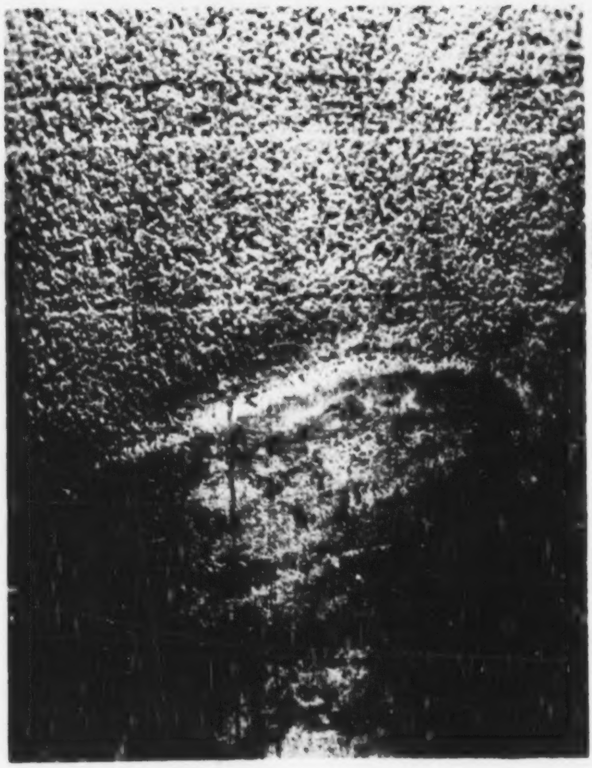

Exposed
Section
Teflon Tape
Protected
Section
7X

Figure 58. Exposed 316L Tube

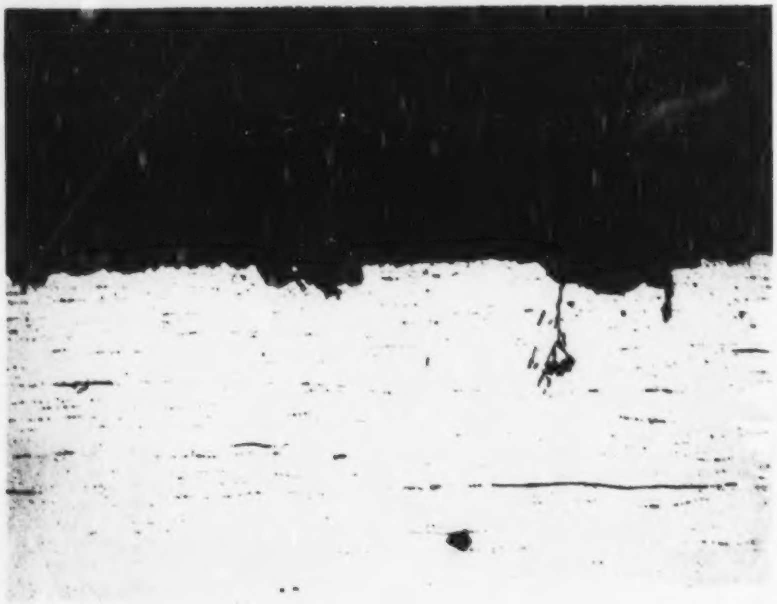


Figure 59. I.D. of Exposed Armco Tubing Showing Some Cracks And Corroded Areas

Figure 60. O.D. of Exposed Armco Tubing Showing Stringers Along The Tube Drawing Axis and Light Pitting

100X

Figure 61. O.D. of Exposed 316L Tubing Showing Corrosion Pits

100X

Figure 62. I.D. of Exposed 316L Tubing Showing Less Severe Corrosion

Table 49 gives change in yield strength and elongation after exposure based on an arbitrary ± 5% allowed variation in yield strength and a ± 10% allowed variation in elongation. The only material that showed significant degradation in both strength and ductility was 316SS.

Table 50 gives a summary of qualitatively observed events during the course of the test. It is evident that most of the 300 series stainless steels showed alarmingly poor corrosion resistance in the desulfurization process environments.

The results of the present study show that the rates of corrosion of the 300 series stainless steels are extremely sensitive to the metallurgical condition of the sample, particularly residual stress. This is brought out dramatically in the case of the 304L tubing (Figure 38) which was completely corroded away due to the built-in stresses in the tube drawing process. It is well known that in an acidic environment, the stresses could cause increase in corrosion rate several-fold especially at temperatures in the region of 100°C. A possible mechanism is the precipitation of carbides and nitrides or agglomeration of C or N atoms at dislocation sites which causes local action cells in plastically deformed material. This is also borne out by the observation that 316 corrodes just outside the weld zone where cooling stresses are greater and the fact that the welded seam in Armco tubing, where some of the drawing stresses must have been annealed out, is free of corrosion.

The cracking observed along the cut edges of 316, 316L, 347 and Armco tubing also is indicative of embrittling due to stress corrosion. The cracking appears to be transgranular, following crack-sensitive paths determined by loci of local action cells formed due to residual stress or cold working. Whether Cl^- ions play a role in aiding stress corrosion by adsorption is not known since the solution has not been analyzed for Cl^- ions. The sorption may occur selectively along paths of pinned dislocations or vacancy-alloying element clusters formed due to plastic deformation or residual cooling stresses after welding. The fact that 304L (extra low

TABLE 49. CHANGES IN MECHANICAL PROPERTIES OF ALLOYS AFTER EXPOSURE TO IRON SULFATE SOLUTION

Material	Yield Strength		Elongation	
	Control ± 5%	Exposed	Control ± 10%	Exposed*
304	45.98 - 50.82	44.5 (-)	35.6 - 43.40	40.0 (0)
316	38.95 - 43.05	36.0 (-)	33.9 - 41.50	30.0 (-)
316L	43.5 - 48.09	45.5 (0)	23.4 - 28.6	26.0 (0)
321	43.2 - 47.80	54.1 (+)	27.9 - 34.1	25.0 (-)
Armco	53.8 - 59.40	60.1 (-)	23.4 - 28.6	22.0 (-0)
Carp	47.9 - 52.9	56.5 (+)	18.9 - 23.1	21.5 (0)
Inconel	70.5 - 77.9	74.5 (0)	19.8 - 24.2	18.0 (-0)
Incoloy	45.7 - 50.5	56.7 (+)	15.3 - 18.7	15.0 (-0)
347	42.5 - 46.9	42.0 (+)	13.5 - 16.5	30.0

---

* (+) indicates increase

(-) indicates decrease

(o) indicates that the values lie within the allowed range

TABLE 50. SUMMARY OF QUALITATIVELY OBSERVED EVENTS DURING CORROSION TESTING

- 304 thermocouple shield tube disintegrated after a short time~s.) (16 hrs) exposure
- 304 screws used initially were severely corroded
- 304L tubing was severely corroded in the composite welded tube
- Type of Corrosion (Plate Materials)

  Pitting type: 316, 316L, 347

  General type: 304, 321, Armco, Carpenter, Inconel, Incoloy

carbon, ELC, grade by Sandvik Corporation was completely corroded away also suggests the above mechanism as no sensitization can occur in the very low carbon grade stainless steel.

The pits seen in 316 and 347 may be due to accelerated corrosion at isolated stress points and/or local action cells due to concentration differences.

The extreme sensitivity of corrosion rates to residual stresses is also apparent from the fact that 304 was considerably more stable than 316 and 347 in sheet form while it was severely corroded in drawn tubes and machined screws.

7.2.4 Conclusions and Recommendations

- 304, 304L and 316 appeared to be marginal as construction materials to be used in the coal desulfurization reactor.
- Dynamic testing in an environment where oxygen is in plentiful supply may improve the stability of some of these alloys.

7.3 DYNAMIC TESTING

A composite welded tube, made up of 1-1/2" sections of tubing of different candidate hardware materials for the coal desulfurization process was tested in the L-R rig for approximately 50 hours of simultaneous coal leach and reagent regeneration. The experimental tubing replaced a section of the flow pipes in the L-R rig; hence the tube interior was exposed to the erosive environment of flowing mixture of coal fines and ferrous/ferric sulfate solution. The objective of this test was to evaluate and compare the corrosion resistance of the various candidate materials under dynamic processing conditions and in the presence of finely dispersed oxygen.

Post-exposure examination was conducted on the test tubing. The tubing was first cut into two halves longitudinally to expose the interior. After cleaning superficial dirt by blowing with compressed air, the different sections were examined with a low power microscope for gross evidence of corrosion. Figure 63 shows a picture of the composite tubing before it was cut. Figure 64 shows the results of low magnification microscopic examinations at various locations. There were no visible changes in areas where no remarks are noted. Faint corrosion spots and adhering stains were observed but no gross corrosion was evident on even the worst area. Figures 65 and 66 show the 304 and Armco sections, respectively, under low magnification. It is evident that no apparent corrosion has occurred in any of the tubing materials.

Three sections were selected for microscopic examination:

(1) 304-Armco weld area

(2) 316-321 weld area

(3) Carpenter 20Cb/3-304L weld area.

Figures 67 through 70 show the microstructure of the parent metal and the weld areas. Intergranular corrosion found in some alloys in previous investigations was not observed in any of the materials evaluated in this investigation. Sensitization (shown as black spots) was seen in the weld areas as shown by the presence of precipitated chromium carbide but corrosion at the grain boundaries is not discernible.

Negligible corrosion was observed for all alloys tested for 50 hours in the coal desulfurization test unit. Apparently, the presence of quantities of available oxygen may inhibit the corrosion of the stainless materials investigated. However, the test duration was too short to be definitive. Much longer times in excess of several hundred hours would probably be required before a measurable amount of corrosion can be observed.

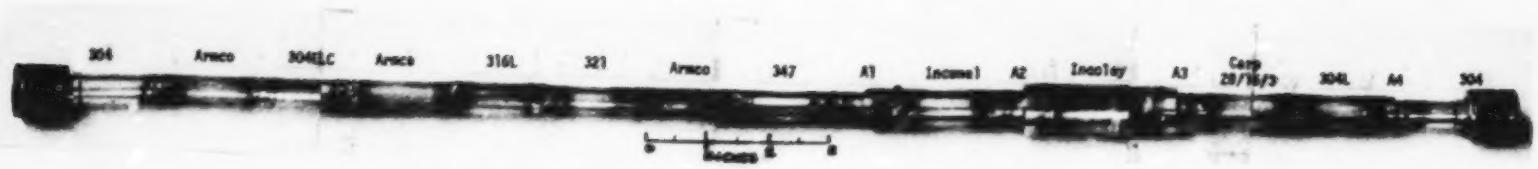

304
Armco
304ELC
Armco
316L
321
Armco
347
A1
Inconel
A2
Incoloy
A3
Carp
20/18/3
304L
A4
304
0
INCHES
4
8

Figure 63. Composite Tube Used in Dynamic Test

Note: two end fittings are 304 SS. Adapters A1 through A4 are 304 SS

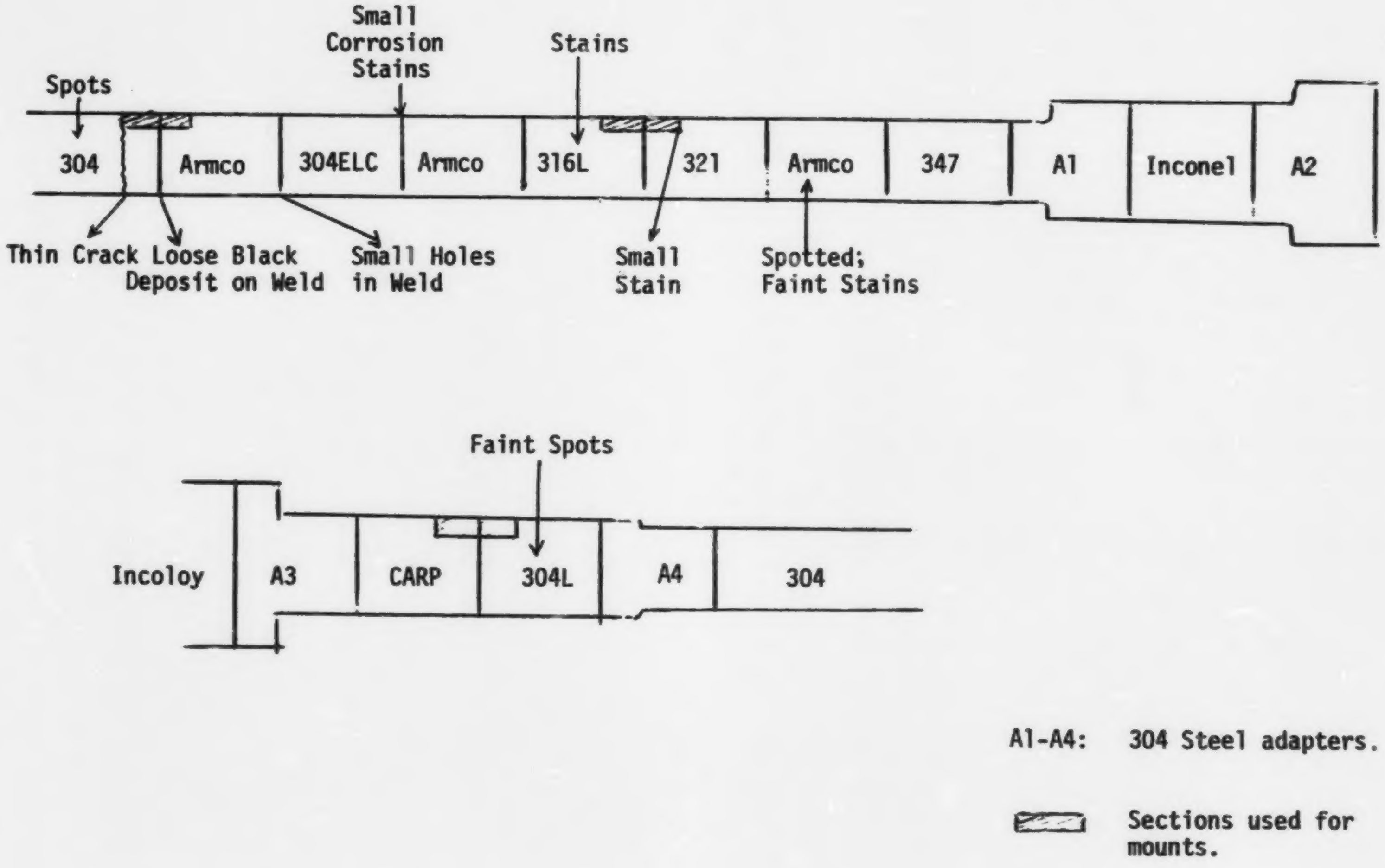

Small
Corrosion
Stains
Stains
Spots
304
Armco
304ELC
Armco
316L
321
Armco
347
A1
Inconel
A2
Thin Crack
Loose Black
Deposit on Weld
Small Holes
in Weld
Small
Stain
Spotted;
Faint Stains
Faint Spots
Incoloy
A3
CARP
304L
A4
304
A1-A4: 304 Steel adapters.
▨ Sections used for mounts.

Figure 64. Composite Welded Tubing: Corrosion Effects in the Tube Interior.

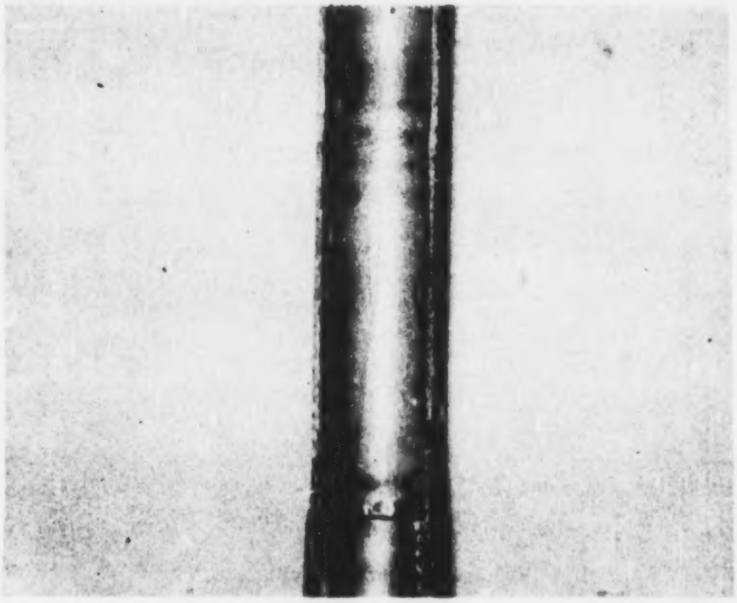


Figure 65. Section of Armco Tubing Interior. No Gross Corrosion Effects

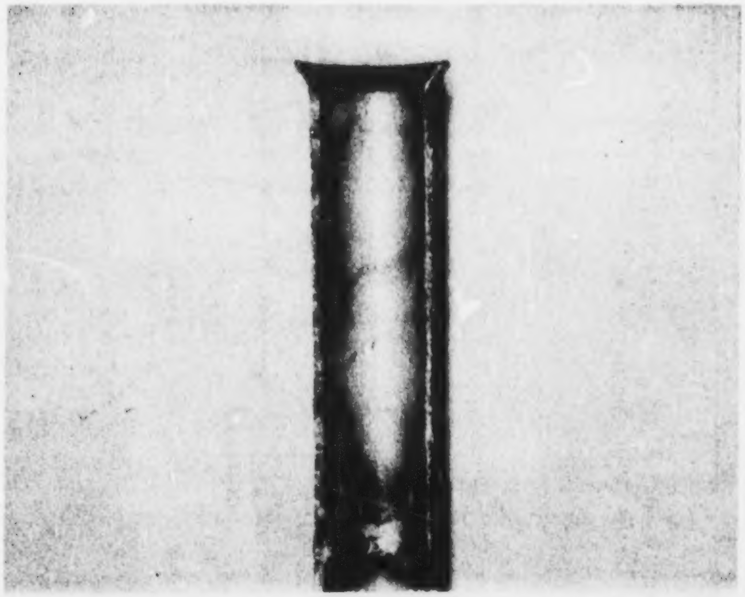


Figure 66. Section of 304 Tubing Interior. No Evidence of Corrosion

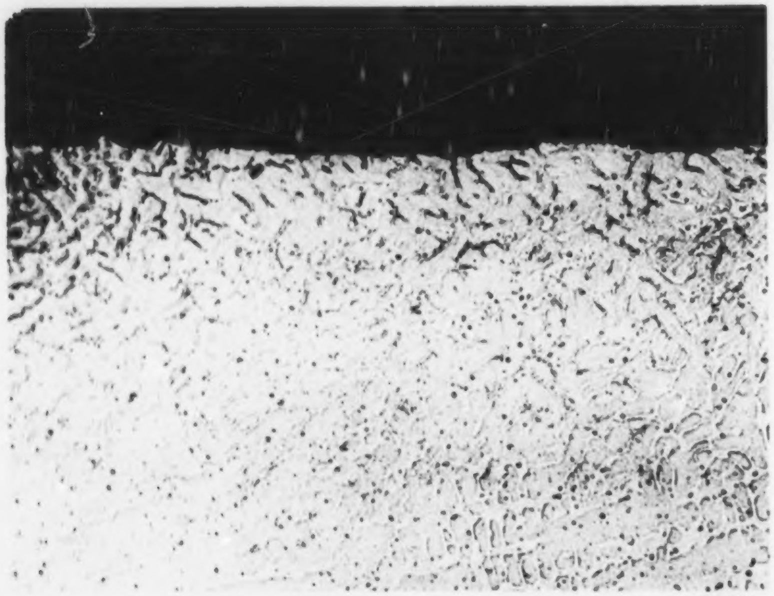

400X

Figure 67. Weld Zone of Armco-304 Showing Chilled Structure and Sensitization by Chromium Carbide

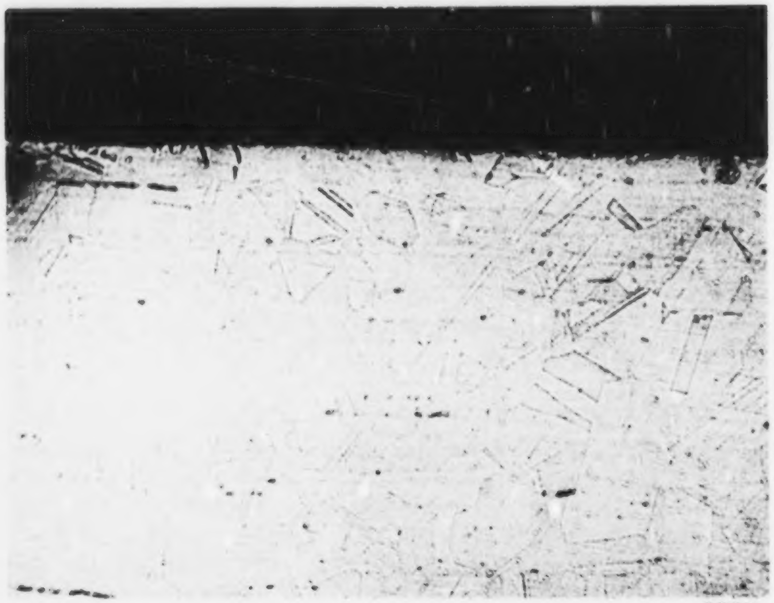

400X

Figure 68. Structure of 304 Away from Weld

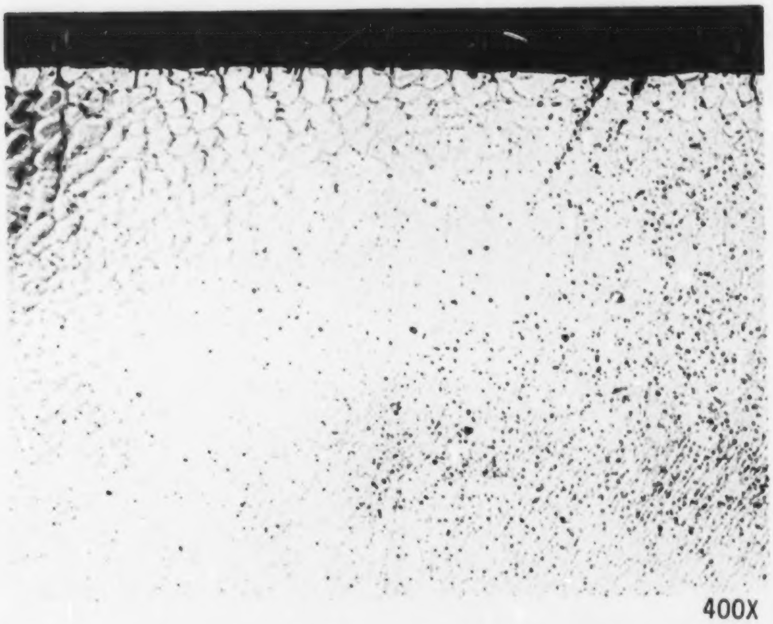


Figure 69. Weld Zone of 316L-321 Showing Sensitization

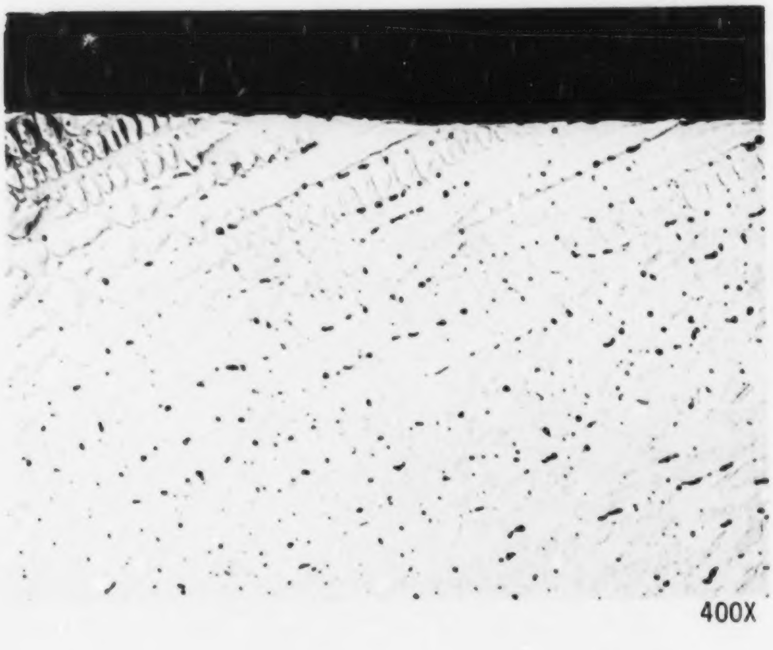


Figure 70. Weld Zone of 304L-Carpenter 20 Cb/3 Showing Chilled Structure and Grain Boundary Sensitization

APPENDIX TO SECTION 7

Corrosion Characteristics of Steel Alloying Elements

Element(s)	Property
Ni + Cr	Resists oxidizing chemicals
High Ni + Mo	Resists non-oxidizing solns
High Mo + Cr/Si + High Ni + Cr	Resists boiling H_2SO_4
High Ni + Mo	Resists fluctuating oxidizing salt solutions
High Co, Ta, Ti, Low C	Resists sensitization during welding
High Ni	Freedom from chloride ion stress corrosion cracking
Mn + High Ni	Improved resistance to pitting, stress corrosion cracking and increased strength and stabilization

APPENDIX TO SECTION 7

CHEMICAL COMPOSITION OF CANDIDATE MATERIALS TESTED IN WT. PERCENT

	Ref	Cr	Ni	Fe	Mo	(Nb+Ta)	C	Ti	Si	Mn
Inconel 625	(17)	20-30	57-60	5	8-10	3-4	0.1	0.4	0.5	
316	(15)	16-18	10-14	Rem*	2-3		0.08		1.0	2.0 Max
316L	(15)	17-21	9-13	Rem	2-3		0.03		1.5	
304L	(15)	17-21	8-12	Rem	-	-	0.03	-	2.0	
Armco 22-13-5	(19)	20-23	11-13	Rem	1.5-3.0	0.1-0.3	0.06 Max		1.0 Max	4.0-6.0
Carp 20-Cb-3	(20)	19-21	32-38	Rem	2-3	8xC-1.0	0.07 Max		1.0	2.0
304	(15)	18-20	8-12	Rem	-	-	0.08		1.0	2.0
321	(15)	17-19	9-12	Rem	-	-	0.08	5xC Min	1.0	2.0
347	(15)	17-19	9-13	Rem	-	10xC Min	0.08	-	1.0	2.0
Incoloy 825	(16)	19-23.5	38-46	Rem	2.5-3.5	-	0.05	0.0-12	0.5	1.0 Max

---

*Rem = remainder

8. REFERENCES

1. Hamersma, J. W., E. P. Koutsoukos, M. L. Kraft, R. A. Meyers, G. J. Ogle, and L. J. Van Nice, "Chemical Desulfurization of Coal: Report of Bench-Scale Developments", EPA R2-73-173 a and b, prepared for the Office of Research and Monitoring of the Environmental Protection Agency, Research Triangle Park, N. C., February, 1973.

2. Hamersma, J. W., M. L. Kraft, C. A. Flegal, A. A. Lee, and R. A. Meyers, "Applicability of the Meyers Process for Chemical Desulfurization of Coal: Initial Survey of Fifteen Coals", EPA-650/2-74-025, prepared for the Office of Research and Monitoring of the Environmental Protection Agency, Research Triangle Park, N. C., April, 1974.

3. Hamersma, J. W., and M. L. Kraft, "Applicability of the Meyers Process for Chemical Desulfurization of Coal: Survey of Fifteen Coals", EPA-650/2-74-025-a, prepared for the Office of Research and Monitoring of the Environmental Protection Agency, Research Triangle Park, N. C., September 1975.

4. "Program for Processes for the Selective Chemical Extraction of Organic and Pyritic Sulfur from Fossil Fuels", Document No. 17270-6011-RO-00, Contract EHSD 71-7, prepared for the Office of Research and Monitoring of the Environmental Protection Agency, Research Triangle Park, N. C., January 15, 1975.

5. Leonard, J. W., and D. R. Mitchell (Editors); Coal Preparation; Am. Inst. of Mining, Metallurgical and Petroleum Engineers, Inc., New York, N. Y., 1968.

6. Guthrie, K. M., "Capital Cost Estimating", in Modern Cost Engineering Techniques, ed. H. Popper, McGraw-Hill, 1970, pp 80 to 108.

7. Mills, H. E., "Costs of Process Equipment", in Modern Cost Engineering Techniques, ed. H. Popper, McGraw-Hill, 1970, pp 111 to 134.

8. Happel, J., and D. Jordan, Chemical Process Economics, 2nd ed., Marcel Dekker, Inc., 1975.

9. Perry, R., and C. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, 1973.

10. "Chemical Marketing Reporter", Schnell Publishing Company, June 2, 1975, p. 44.

11. "Final Report - The Supply-Technical Advisory Task Force - Synthetic Gas-Coal", prepared by the Synthetic Gas-Coal Task Force for the Supply-Technical Advisory Committee, National Gas Survey, Federal Power Commission, dated April, 1973.

REFERENCES (CONTINUED)

12. Barringer Research Ltd., Rexdale, Ontario, Canada, "Feasibility Study for Sensing Sulfides in Coal", Final Report, Natl. Center for Air Pollution Control Contract, PH86-67-270, Proj. 385, Report TR-68-55.

13. Comparison of Oxidation and Reduction Methods in the Determination of Forms of Sulfur in Coal: Environmental Geology Notes #66, Illinois State Geological Survey, December 1973.

14. Hurley, R. G., and E. W. White, New Soft X-Ray Method for Determining the Chemical Forms of Sulfur in Coal, Anal. Chem., Vol. 46, #14, December, 1974.

15. "Corrosion Resistance of the Austenitic Chromium - Nickel Stainless Steels in Chemical Environments". The International Nickel Co., N.Y., 1963.

16. Incoloy 825 Spec Sheet, Huntington Alloy Products Division, International Nickel Co., Huntington, W. Virginia.

17. Inconel 625 Spec Sheet, Huntington Alloy Products Divisions, International Nickel Co., Huntington, W. Virginia.

18. Hastelloy C-4 Spec Sheet, Cabot Corporation, Kokomo, Indiana.

19. ARMCO-Product Data Bulletin S-45a, Armco Steel Corporation, Baltimore, Md.

20. CarTech Selecting Carpenter Stainless Steels, Carpenter Tech Corporation, Reading, Pa.

9. GLOSSARY OF ABBREVIATIONS AND SYMBOLS

Abbreviations

Abs	absolute
ASTM	American Society of Testing Materials
btu	British Thermal Unit
cal	calories
eq	equation
Exp.	experiment
Kcal	kilocalories
No.	number
wt	weight

Symbols

A_L	Arrhenius constant in leach reaction (hours)$^{-1}$ (wt% pyrite in coal)$^{-1}$
A_R	Arrhenius constant in regeneration reaction (minutes)$^{-1}$ (atm)$^{-1}$ (liters/mole)
C	concentration
Δ	difference in quantity following delta
E_L	activation energy for pyritic sulfur leaching reaction, Kcal/mole
E_R	activation energy for ferric ion regeneration reaction, Kcal/mole
K_L	pyritic sulfur leaching rate constant (units same as A_L)
K_R	ferric ion regeneration rate constant (units same as A_R)
μ	micron.
P	total pressure, atmospheres
P_{O_2}	oxygen partial pressure
R	gas constant, cal/mole, °K
r_L	pyritic sulfur leaching rate, weight of pyrite removed per 100 wts of coal per hour
r_R	ferric ion regeneration rate, moles per liter per minute

Symbols (cont'd)

S_n	elemental sulfur
S_o	organic sulfur
S_p	pyritic sulfur
S_s	sulfate sulfur
S_t	total sulfur
T	absolute temperature, °K
t	time, hours (leaching)-minutes (regeneration)
W_p	pyrite concentration in coal, wt%
Y	ferric ion to total iron ratio